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PREFACE

The workshop on the "Black Sea Fluxes" was organized by the IOC-BSRC and the Institute of Marine Sciences and Management of İstanbul University (IU-IMSM), with the participation of the Southern Branch of the Institute of Oceanology, Russian Academy of Sciences. The meeting was sponsored by the IOC and the IU-IMSM, and held at the IU-IMSM on 10-12 June 1997. The three-day Workshop involved the presentation of papers and meetings of working groups to discuss the planning of the IOC-BSRC Pilot Project 2, "Assessment of the Sediment Flux in the Black Sea: Mechanisms of Formation, Transformation and Dispersion, and Ecological Significance".

During the workshop, 15 scientific papers were presented. Nine of the papers were on fresh water, sediment and various pollutant fluxes by rivers; two papers on the fluxes of nutrients and heavy metals via the Bashers; one paper on the atmospheric pollutant input measured in the Turkish Black Sea coast; one paper on the results of a sediment trap study in the southern Black Sea; one paper on the composition of organic particulate matter in the water column and sediments; and another one on the GIS study for the Black Sea. Two of the presentations dealing with the riverine sediment fluxes, also presented data on the coastal and near-shore processes of erosion and sediment transport. Fourteen of these presentations have been submitted in full manuscript for publication in the present volume.

The main results of these papers can be summarized as follows:

(i) Data on the riverine sediment and pollutant loads, and the flux calculations through the Bosphorus indicate that the riverine inputs, and in particular the loads via the river Danube, constitute a major part of the total fluxes into the Black Sea. The new results also show that the sediment input by the Turkish rivers has decreased from 53×10^6 t/y to 24×10^6 t/y because of new dam construction during 1980s.

(ii) The preliminary aerosol data from the Turkish Black Sea Coast shows that the atmospheric input of pollutants represents a significant portion of the total input. The data also shows that the atmospheric pollutant input is higher in the western part of the Black Sea, indicating a substantial European influence.

(iii) The study of sedimenting organic matter in the oxic, suboxic, and unoxic zones of water column as well as research in its early diagenesis in the sea floor sediments is essential for the understanding of the biogeochemical cycles and organic fluxes.

(iv) Preliminary flux calculations concerning nutrients and dissolved heavy metals through the Bosphorus indicate that there is a net pollutant input of dissolved metals and nutrients from the Black Sea into the Sea of Marmara (and the Aegean Sea), causing eutrophication problems in these neighboring seas. However, considering that a major fraction of the studied metals, such as Fe, Mn and Pb, is in colloidal form, a flux study involving "total" metal analysis in the Bosphorus and Çanakkale (Dardanelles) straits, is deemed necessary.

This workshop volume, therefore, includes some important new data, filling in the gaps in the flux estimates. It also brings to one's attention the following priority areas for further research, related to the objectives of the Pilot Project 2:

1. Time-series measurement of the amount and composition riverine and aerosol fluxes. Study of biogeochemical cycles and organic fluxes in the oxic, suboxic, and unoxic zones of water column, and investigation of early diagenesis of organic matter in the sea floor sediments.

2. Study of sediment cores to determine changes in sedimentation rates, organic-matter fluxes, and climate and in oceanographic conditions in the recent geological past of the Black Sea.

3. Study of suspended matter fluxes using satellite observations.

4. Compilation of new maps of land-based sediments and pollutant fluxes into the Black Sea.

5. Development of a common database system for the use of Pilot Project 2, in line with the international DATABASEs, such as WYCOS/MEDHYCOS and FRSEND-IMFAM.

In conclusion, I would like to offer my personal thanks to my fellow contributors for their cooperation in producing this volume, to the members of the IU-IMSM for their help in organizing this symposium, and to Dr. Oya Algan for her help in formatting this volume. I hope that this volume will be a valuable contribution to the future sediment- and pollutant-flux studies in the Black Sea.

Istanbul, August, 1998

Namık Çağatay

BLACK SEA – THE BEGINNING OF 4D OCEANOLOGY

By Prof. A.P. LISITZIN, Member of the Russian Academy of Sciences,
Head, Laboratory of physico-geological studies of P.P.Shirshov Institute of Oceanology RAS

The study of heat and salt fluxes was a traditional tendency of oceanology during many years. At the end of the twentieth century, the study of suspended matter fluxes in sea water was added to these investigations. Lithology and geochemistry of suspended matter in the ocean and the sea can now be successfully established, and their physical properties and connections with solute and colloid forms and with biological processes and with properties of the water column can be studied. Sedimentary trap is the main instrument for the research of fluxes. The results of such investigations have been summarized in a number of monographs published in recent years. Important multi-year investigations have been carried out in the Black Sea. This new trend in the study of the World Ocean has a practical application, especially when investigating an anthropogenic stress and pollutant transport in the ocean. But, to my mind, only the very initial tasks of such a research have been fulfilled and its vast potential capabilities have not yet been fully utilized. I will briefly examine below the prospects of study of suspended matter fluxes in the sea and in particular the role of the Black Sea in such investigations.

Unfortunately, today the study of suspended matter and its fluxes has a static character. Such a research, if supplemented with a complex of appropriate observations and instruments, can become the basis of a major evolution from the present 3D oceanology to a future 4D oceanology, by using the additional time factor.

Usually, seasonal changes of oceanological processes are considerable, and short-time observations performed during research expedition cruises may be likened to a snapshot photography of the process, capturing a short glimpse of the processes and events mostly during favorable weather conditions. For example, in the Arctic almost all the data pertain to only 2-3 summer months and information about the processes during most of the year (9-10 months) is scanty.

Traps installed at different depths collect samples by intervals of 15-30 days. They serve as original clocks or time machine and enable the oceanologists to study oceanological processes all year round or for decades if the instrument installation is a more durable one. Today, the records of the environmental parameters recorded in sediment trap samples can be interpreted incompletely. When working in the Arctic, we used biological methods of interpretation on the basis of a detailed study of microscopic remains of planktonic organisms as well as spores and pollens of plants. Geochemical methods and the mineralogical analysis of clastic and clay minerals are also used rather widely. The next stage is the precise analysis of organic matter, namely biomarkers, isotopic composition of suspended matter, etc. Since the weight of samples collected in the traps is usually insufficient, it is necessary to use rather sensitive and most advanced analytical methods.

A combination of these and other methods of research provides a possibility to reconstruct the environmental conditions in time, as the suspended sedimentary material is a self-recorder of environmentally important oceanographic parameters. The most effective application of the suspension and flux studies for 4D oceanology would be achieved when used in combination with some other instruments: firstly with current meters and devices which determine temporal fluctuations in suspension concentration.

A precise assessment of the temporal changes in water currents is possible when current velocity meters are used. Installed at different depths, they record at a certain time interval and store them in the computer memory. The other possibility is to use a stationary Doppler currentmeter with programme controller that can measure current velocity at different water depths in a given time interval.

Temporal variations of the quantitative content of suspended matter can be recorded using autonomous transparency meters deployed at different depths at the same station. This allows to monitor not only vertical, but also horizontal and inclined fluxes of matter (vectors) and their temporal and spatial fluctuations at different depths.

To study temporal fluctuations of temperature and salinity, it may be necessary to install Nale-Brown self-recorders with a programme controller. Such a set up would be especially useful in complex marine environments, such as estuaries, where a complex, temporally variable water column structure exists.

Thus, the research of the suspended matter fluxes can initiate a new trend (i.e., 4D oceanology) in oceanographic studies, involving marine geology, biology, chemistry and ocean physics. A system of such stations established within a certain basin would ensure the acquisition of a complete and reliable data set at the highest level, which had not been accessed before.

The study of material fluxes connected with all aspects of the marine environment is not confined to the sediment trap and related studies. The second and equally important line of studies has the capacity to determine longer-term (at scales of tens, hundreds and thousands of years) variability in natural processes in the sea. It is the study of paleofluxes, which represents another aspect of 4D oceanology. The understanding of cycles, frequency of catastrophes and anomalies in the past is necessary for the assessment not only of the past and present processes, but also for future forecastings. Here, we use bottom sediments which are the natural self-recorders of the processes and events in the sea. The study of paleofluxes in the sediment column, namely the rates of sediment accumulation, together with a detailed study of the trap material collected in the same region, reveals great possibilities for 4D analysis, by providing time-series data for the last tens to thousand years. It is clear that we must learn to read these records and reveal their breaches and distortions.

One of the most important problems is the identification of the cyclic nature of climatic changes. For instance, whether the rise in temperature is connected with the greenhouse effect or, to my mind as a more logical explanation, it is a natural global process of cyclic fluctuations in heating, as revealed in the sediment and ice cores. The increase in the carbonic acid and thermoactive gases may be an accidental coincidence with the more powerful natural factors of cyclic global changes of climate. When studying sections of bottom sediments, one could also determine the pollutant stratigraphy and history of anthropogenic impact upon the ocean.

Thus, in the Baltic Sea the basic epochs of the evolution of civilization for the last two thousand years were determined when studying the pollutants. These epochs, from top to bottom, are the periods of atomic energy, automobile, paper, agriculture, etc. The pollution history of every basin recorded in the bottom sediments and compared with the modern fluxes provides a series of long-term observations and constitutes the basis for a sound prognosis.

Very likely, the strategy of research will change in the course of 4D investigations in view of the prevalence of (short-term) observations carried out on board research vessels on the observations made at the sediment stations, coupled with the analysis of critical samples of bottom sediments.

The new method of investigation is rather expensive and requires the establishment of a sufficient number of sediment stations. Therefore, it would seem logical that a division of the studied marine basin into a number of regions be made on the basis of all oceanological information, each region representing an oceanographically distinct part of the basin in terms of environmental conditions. For example, in the Black Sea such an initial subdivision could include the eastern and western halistazes, the northwestern part (under the predominant influence of the Danube River); the northeastern and the Caucasian parts as well as the coastal regions of Turkey, giving a total of 5 regions. A station for long-term observations would be installed in the most characteristic part of each region. Data obtained at this station should be supplemented by cruise data and observations when of changing the station supply. This requires a combination of complete oceanological, physical, chemical, biological and geological investigations carried out by research groups, at a maximum density within the polygon where the station is situated, and on a more sparse net away from the polygon.

A summary picture for this basin is built up when data from every region are integrated. If necessary - for example, when studying pollutants in a certain region - a general strategy of investigations is supplemented with more detailed works on the routes of pollutant distribution from the source to the boundaries of the polluted region. The strategy of investigations and is lilely to change considerably, as new data are obtained and instruments developed.

It is now necessary to use satellite data for the determination of the intensity of biological processes and their temporal fluctuations. This concerns the study of an assimilative pump, the phytoplankton, which transfers dissolved nutrient matter into suspension, and of a second pump, zooplankton which, by feeding on the phytoplankton, serves of filter for the upper layer of the ocean and produces pellets. In future sedimentary stations, this system will be obligatory for the verification of satellite data obtained all the year round (in contrast with cruise observations).

Eolian material constitutes a sizable and sometimes the basic part of suspended matter fluxes in seas and oceans. According to recent data, air suspension is the most important source of biogenic elements, since their flux from the atmosphere determines the intensity of the biological pumps. The Eolian transport is an important pathway for transfer of sedimentary material (from 10% to 90% out of the total amount) and different pollutants. Catastrophic avalanche blowouts of sedimentary material are associated with eolian material, for instance, when the soil is scattered in the Azov-Black Sea regions (black storms) and in the arid part of the Atlantic Ocean.

The study of the fluxes of eolian material must be an integral part of the suspended matter flux observations, an important part of 4D oceanology. It is not necessary to deploy at sea traps for eolian material collection, though such work is highly advisable. At the initial stages, we may be limit to shore-based stations for the study of atmospheric matter fluxes involving the analysis of both solid and dissolved matter. Such round the year observations in the shore observatory can be supplemented with the study of aerosol samplings during cruises on the polygons where 4D sedimentary stations with traps are deployed.

There are several important reasons why the Black Sea seems to be the most interesting marine basin for the study of sediment fluxes and the development of 4D oceanology. First, the water area of the Black Sea is situated at the boundary of arid and humid regions with their own peculiarities of flux and sediment formation. The role of eolian material is very appreciable here and therefore, within single basin the data for two important climatic zones occupying more than half of the total World Ocean area, can be obtained.

Secondly, the Black Sea is the largest stagnant basin in the World. The process of intermixing here is weak, and hydrogen sulfide in deep waters promotes the safe preservation of unstable components of the suspension. The horizontal transport of suspended matter is weaker than in the other seas and basically ioccurs in the shelf regions only.

Thirdly, the Black Sea is a solar sea. Here, we have very good conditions for the use of satellite oceanology, especially for the SeaWifs data, whereas in the Arctic, for instance, the sea surface is hidden by clouds or covered with ice during the largest part of the year.

Numerous marine research institutions and laboratories in many countries are situated on the Black Sea shore. They are expert in marine research, having already gathered a large amount of relevant data. They also understand the need for promotion from 3D oceanology to 4D oceanology.

To my mind, international investigations within the framework of the IOC-BSRC (UNESCO) Pilot Project 2 in the Black Sea may have in this case a considerable impact during a relatively short time. The articles collected in this volume are a testimony for the future success of this research project.

FLUXES OF SEDIMENTS AND POLLUTANTS IN THE BLACK SEA

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ABSTRACT

The rivers are the main sources both of sediments and pollutants. Their irregular supply from different catchment areas controls the nature of terrigenous sedimentation and contamination of the Black Sea. The role of aerosols in the Black Sea has not yet been estimated.

As a result of studies in the Black Sea pre-Caucasian zone, it is revealed that fluxes of sediments and pollutants display a wide range of temporal and spatial variations. The spotty character of their spatial distribution in shallow water areas is conditionsed by peculiarities of the water ciruclation. Noticeable amounts of pollutants are accumulating in some areas of semi-enclosed bay; due to the strong anthropogenic contamination carried by small rivers. The continental rise is the main place of acucmulation of sediments and pollutants on deep basin areas of the Black Sea.

Studis performed using sediment traps have revealed that fluxes of sediments and pollutants are much higher in near bottom waters of the shelf, in comparison with their rates of accumulation on the sea floor. A reverse picture is observed on the continental rise of the southwestern deep-sea basin.

Additional data are required for budget estimations of both sediments and pollutants in the whole basin.

INTRODUCTION

The Black Sea is unique for studying contamination processes in a deep and stagnant marine environment. Such investigations are of great importance considering its critical ecological state, because of its increasing anthropogenic pollution (Keondzhan, 1990; Fabry et al., 1993; BSEF, 1996) and the insufficient scientific data for forecasting its future ecological state. The budget assessments of the pollutant circulation in the process of sediments genesis in the seasonal and multi-annual terms can serve for such a purpose. Such assessments have not been done, however, because of insufficient data on the sediment and pollutant fluxes in the Black Sea. Up to now precise data on river runoff from the watershed are not available. The studies of the matter fluxes in form of aerosols and suspended material are at an initial stage, although in the last decade some success has been achieved in technical and methodological aspects for future work in these areas.

This paper has for objective to summarize the main results of flux studies in the Black Sea, with a view to access the present picture and determine the priority tasks for future studies.

FLUXES FROM THE CATCHMENT AREA

Sediments

The river sediment discharge from the watershed is rather irregular. The greatest discharge comes from the northwestern region, drained by the largest rivers of the Black Sea basin: the Danube, the Dnieper and the Dniester (Fig. 1). A relatively small part of the discharge is issued from small rivers of Crimea, Bulgaria and the northwestern Caucasus. The mountain watershed of Turkey and Georgia is in a middle position in terms of the amount of the river runoff. Such a picture was revealed long ago (Shimkus and Trimonis, 1974) and has been confirmed by subsequent investigations (Jaoshvili, 1986), though accurate estimates of water and sediment runoffs slightly differ from each other.

The river sediment runoff has strong annual fluctuations which have been studied best of all for the northwestern (Danube, Dnieper, Dniester, Bug) and northern rivers (Don, Kuban) (Panin, 1996: Polonsky, 1995).

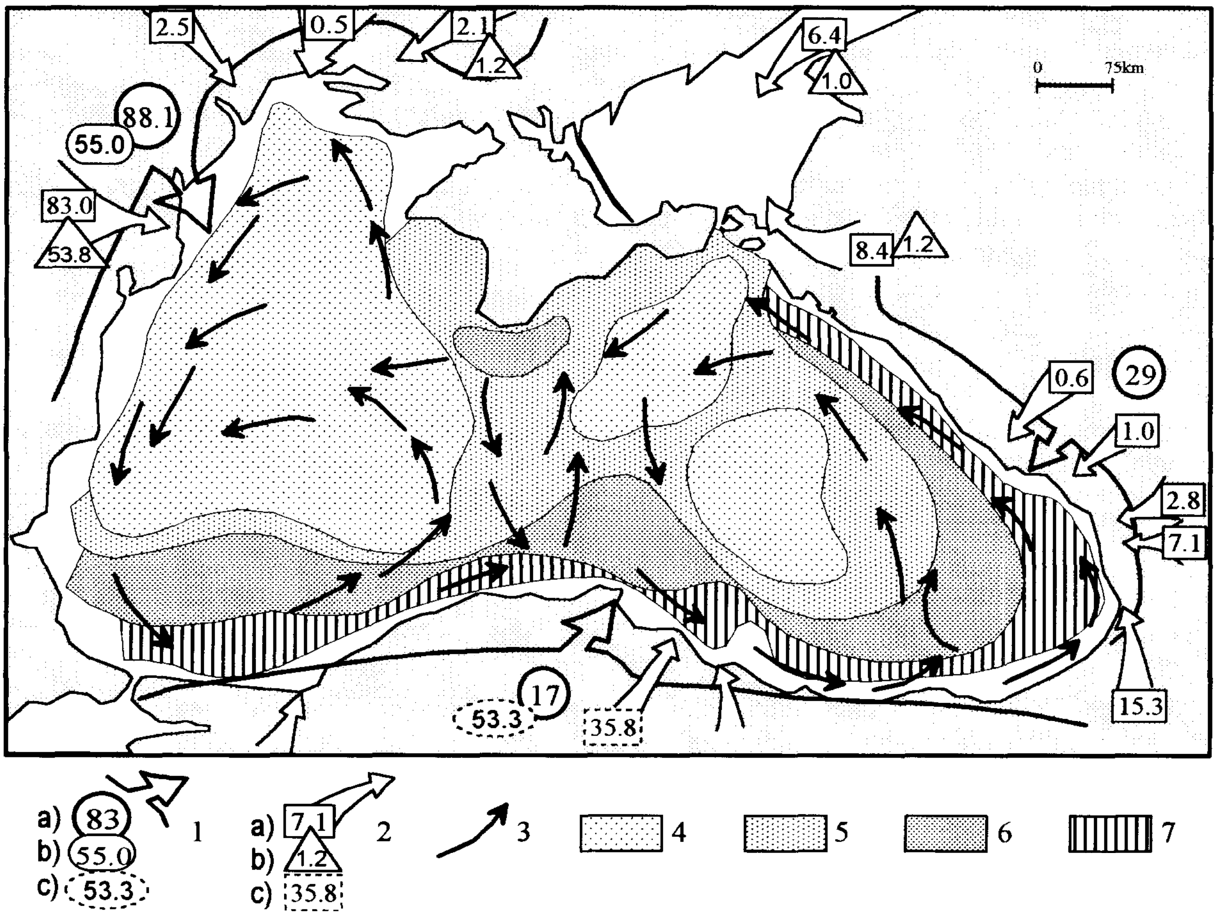

FIGURE 1. Annual river supply of sedimentary material to the Black Sea and rates of recent sedimentation (0-3 k/yr).

1 – annual river solid load from separate catchment areas ($n \cdot 10^3$ tons/yr):

a) - mean values before rivers' artificial regulation (Shimkus and Trimonis); b) - mean values after artificial regulation (Bondar and Blenda, this volume]; c) - modern flow after O.Algan et.al., this volume.

2 – that one of some separate rivers:

a) - mean values before rivers' artificial regulation (Shimkus and Trimonis, 1974); b) - mean values after artificial regulation (Shimkus and Trimonis, 1974; Trimonis, 1975); c) - modern flow after Algan et.al. (this volume).

3 – surface water currents;

4-7 – rates of sediment accumulation (after .Shimkus, 1993) (cm/k.yr): 4 – <10, 5 – 10-40, 6 – 40-80, 7 – high variation of the rates.

Nearly in a centenary historical cycle, the Danube runoff periodically increased by 1.5-2 times, compared to the present time (Polonsky, 1995). Its maximum values have been observed during periods of increased humidity in 1940-41, 1955, 1967 and 1980. In these relatively wet periods the Danube River sediments played a major role in the Black Sea sedimentogenesis, but between these intervals their importance dropped sharply. A modern picture confirms this. During the last decades the Danube solid runoff is within 40-50 10^6 t/yr (Panin et al., 1990).

During the last 50 years the river runoff reduced considerably due, not only to the climate aridity, but also as a result of the construction of dams and the increased use of water for irrigation. After the construction of the Tsymlyanskoe Dam in 1953, the water runoff of the Don has been reduced by 50% and, its total solid load by 75%. The Krasnodar Dam, completed in 1973, decreased the Kuban River's solid runoff by about 90%. After the construction of the hydroelectric power station on the

Inguri river (1978 yr.), the runoff of a beach-forming material has been reduced by 92% [Jaoshvili, 1986). Large losses of solid runoff (about 45%) from the northwestern watershed were provoked by the building of dams for hydroelectric power stations and numerous systems of irrigation on the Danube (Panin, 1996) and the Dniester rivers. As a result of the river regulation, the losses of the river sediment runoff is estimated at 19-25%, with a possible increase of this figure up to 52% in the future (Fabry et al., 1993). There are important seasonal fluctuations of the river runoff, and they vary in the different regions of the watershed.

The northwestern rivers are characterized by a spring maximum (march-may) and a small peak in autumn. In spring, the danube runoff increases by 1.5 times. the maximum values from spring to early summer (april-june) are typical for the largest rivers of the georgian watershed (jaoshvili, 1986). The two maxima runoffs of the turkish largest rivers, such as yeşiirmak, çoruh and sakarya, were observed in spring (may) and autumn (october). the kızılırmak river keeps aloof; its runoff reaches the maximum values in in summer (july). Owing to the temporal and seasonal maximum shift of the river runoff, both in the northwestern and southern regions, the watershed has a great influence on the sedimentogenesis and ecological situation in the basin.

Fluxes of sedimentary material from the watershed not only vary quantitatively, but also in the granulometric composition. pelitic fractions (<0.01 mm) prevail in suspension of the plain rivers (dnieper, don); they represent 42.4 to 91.0% of the total river solid discharge. In mountain/plain rivers (kuban, danube), the fraction of sandy-silty material increases considerably, and in the predominates in the mountain caucasian rivers (shimkus and trimonis, 1974). A total flux of the river sediments consists mainly of fine-dispersed suspended material, with lesser amounts of coarse-grained bed-load material. In the caucasian rivers, it reaches 32% of the solid runoff (hmaladze, 1978).

It should be noted that fluxes of river sediments of different granulometric composition have not yet been calculated, due to the lack of data on the granulometric composition of suspended and tracked material in the Black Sea. the northwestern rivers supply more silty material in suspension compared to clayey fraction. silt fractions exceed more frequently clay fractions in river-suspension of the caucasian watershed in comparison with the danube, the dnieper and other rivers (trimonis, 1975).

Aerosols

There is a lack of data on aerosol material in the Black Sea regions. However, irregular supply of aerosols from the Sahara to the Black Sea is defined as a result of multi-annual satellite observations. The Sahara dust flux in the Western Black Sea on 10 of March 1991 was 0.5-1.0 g/m^2 (Dobricic, 1997). Its abundant spill was observed by the author on 4 of March 1979 in Gelendzhik and by the Georgians in Tbilisi , on 10 of March 1979.

Pollutants

The large rivers of the northwestern catchment area (Danube, Dnieper and Dniester) are the main transporter of pollutants to the Black Sea, because of their important amount of contaminated water discharge (Keondzan, 1990; Minkoskaya, 1996; Polykarpov et al., 1994; Zaitsev, 1992, 1993) (Table 1, 2). It should be emphasized that the existing estimates of pollutant fluxes from the watershed are only tentative, and do not include the pollutant fluxes from the Turkish watershed, which may be very noticeable.

TABLE 1. Average annual input of some pollutants into the Black Sea from the northwestern catchment area (Zaitsev, 1993).

Pollutants	Tons	t/km^3	t/km^2
$N\text{-}NO_3$	570,000	1.60	1.35
$P\text{-}PO_4$	140,000	0.26	0.33
Organic matter	9800,000	18,3500	23,1700
Oil products	206,000	0.39	0.49
Hg	0.082	$0.10x10^{-6}$	$0.10x10^{-6}$
Zn	12,000	0.0200	0.0280
Cr	1,500	0.0028	0.0035
Pb	4,500	0.0084	0.0106
Detergents	48,000	0.0899	0.1135
Phenol	2,200	0.0041	0.0052

TABLE. 2. Volumes of sewage waters supplied from different catchment areas (Polykarpov etal., 1994).

Catchment area	km^3/yr
Northwestern	20.0-25.0
Crimea	1.0-1.1
Caucasus (Anapa – Batumi)	0.5-0.7
Turkey	2.0-2.5
Northern (through the Sea of Azov)	3.5-5.0

The Caucasus drainage area is characterized by a lower distribution of pollutants into the Black Sea, compared to the northwestern catchment area, because of the lower river discharge and waters less contaminated of river waters in the Caucasus, except for those crossing the resort towns and regions of high industrial development, such as Tuapse, Sochi, Suchumi, Poti (Glumov and Kochetkov, 1996). Oil refinery plants, maritime petroleum transport, agricultural and mining activity related to Mn extraction (Georgia) are the main sources of different pollutants in the Caucasian zone of the Black Sea. An uneven river discharge results in supply of pollutants from the Anapa-Tuapse watershed area, with larger amounts from Tuapse-Sochi, and the more important ones from the Sukhumi-Batumi region. The concentrations and fluxes of heavy metals (HM) illustrate this point (Table 3, 4).

TABLE 3. The contents of heavy metals (HM) in riverine suspended matter from catchment area of the Northwestern Caucasus (Shimkus et al., 1996).

River	Collection	%		$x\ 10^{-4}$ %					
	date	Fe	Mn	Cu	Zn	Pb	Cd	Co	Ni
Tsemes	05.93	2.70	0.192	81	472	300	4	28	54
Su-Aran	09.90	-	-	82	512	157	16	-	-
Ashamba	04.89	1.10	0.123	333	205	359	10	-	20
Aderba	05.93	2.00	0.030	69	401	40	2	24	38
Pshada	05.93	4.20	0.048	65	261	60	3	22	70
Ashe	05.93	5.10	0.067	77	500	50	3	33	68
Shakhe	05.93	5.40	0.092	52	354	30	1	16	73
Dagomys	05.93	4.00	0.104	207	532	70	4	23	64
Sochi	05.93	5.60	0.116	70	272	50	3	16	70
Mzymta	05.93	5.40	0.077	52	248	50	13	24	65
Bzyb	04.71	4.60	0.069	78	450	10	-	30	70
Inguri x	04.71	4.70	0.052	53	116	61	-	15	56
Rioni x	04.71	4.00	1.64	62	190	82	-	20	145
Çoruh	04.71	4.40	0.048	89	115	52	-	19	68

TABLE 4. Annual fluxes (t/yr) of particulate heavy metals from different parts of the Caucasian drainage area (Shimkus et al., 1996).

Watershed Region	Suspended matter nx10^3	Fe	Mn	Cu	Zn	Pb	Cd	Co	Ni	Cr
Anapa – Dzubga	264	7181	238	44	96	38	1,7	6	15	-
Tuapse	676	2825	446	38	233	51	1,4	20	40	-
Sochi	1298	66190	1160	123	457	65	6,9	26	88	-
Bzyb	862	39650	7750	67	388	9	-	26	60	91
Kodori	1328	41160	5310	96	396	105	-	32	57	88
Poti – Batumi	21837	952093	126655	1485	3057	1419	-	393	1965	1791

Different pollutants are transported by rivers, both in soluble form and suspended matter. Petroleom products (OP), polyaromatic hydrocarbons (PAH) and some groups of pesticides (PS), RN and HM flow into the basin, mainly in particulate form adsorbed on a fine grained suspended matter, such as clays and organic matter, and Fe-Mn-hydroxides.

The proportion of HM increases in suspended matter, with a raise of the total concentration of the suspension, associated with the floods of river water in spring/early summer and autumn (Table 5).

TABLE 5. Average concentrations (µg/l) and fluxes (t/yr) of the heavy metals in the rivers water discharge of the Sotchi-Tuapse drainage area (Shimkus, 1996).

	µg/l								t/yr							
River	Pb		Zn		Cu		Hg 10^{-3}		Pb		Zn		Cu	Hg 10^{-3}		
	SP	A	SP	A	SP	A	SP	A	SP	A	SP	A	SP	A	SP	A
Psou	3.3	5.8	4.3	137.0	2.8	3.5	23.9	11.1	2.0	3.5	2.9	83.7	1.7	2.1	76.7	0.6
Mzymta	2.1	1.0	16.4	96.4	1.9	2.4	15.2	1.3	3.1	1.5	24.2	142.4	2.8	3.5	22.3	1.9
Sotchi	2.8	1.0	9.2	252.0	3.7	3.6	8.8	1.5	1.6	0.6	5.4	146.6	2.2	2.1	5.1	0.8
Shakhe	1.8	1.0	12.4	243.0	1.9	1.6	10.8	1.8	1.9	1.0	13.2	263.3	2.0	1.7	11.5	1.9
Psezuapse	3.2	4.6	7.1	106.0	2.7	2.2	8.7	1.1	1.6	2.3	3.5	52.0	1.3	1.1	4.3	0.5
Tuapse	1.8	1.1	7.0	159.7	1.6	0.6	19.7	1.8	0.7	0.4	2.7	62.3	0.6	0.2	7.9	0.7

In spring, more noticeable rise of concentrations in river waters is observed as regards pesticides as well as Cu, Zn, Hg (Table 6), due to the chemical treatment of gardens and vineyards. On the Sochi-Tuapse section of the watershed area , OP and PAH fluxes are higher in autumn than in spring.

In the river water from the Sochi-Tuapse watershed, Zn displays direct correlation with oil-products. Strong direct correlation is expressed for Hg and pesticides. The correlation is weaker between Pb and oil-products. Cu and Cd keep aloof and have no correlation with the other pollutants. Such correlation may suggest that a considerable part of Zn and Pb is brought to the sea together with oil-products, and Hg with pesticides. Pesticides and Hg have strongly pronounced seasonal fluctuations with the maximum concentration occurring in spring. Seasonal fluctuations of Cu are less pronounced.

TABLE 6. Seasonal concentrations and fluxes of the pesticides (PS) and oil products (OP) in river water discharge of Sochi-Tuapse watershed (Shimkus and Komarov, 1994, 1996).

River	PS, n x 10^{-6} mg/l		OP, n x 10^{-3} mg/l		PS, t/yr		OP, t/yr	
	SP	A	SP	A	SP	A	SP	A
Psou	29.0	9.0	47.5	153.3	17.7	5.5	29.1	93.6
Mzymta	41.0	6.5	70.0	72.5	60.5	9.6	103.4	197.1
Sochi	127.3	14.4	12.0	20.0	74.1	8.4	7.0	11.6
Psezuapse	64.6	51.1	30.0	30.0	31.7	25.2	14.7	14.7
Tuapse	52.0	12.7	25.0	401.5	20.3	4.9	9.8	156.4
Average	62.8	18.7	36.9	135.5	40.9	10.7	32.8	94.7

Comments: SP - spring, A - autumn

FLUXES IN THE BLACK SEA WATER COLUMN AREA

Sediments

Shallow water area

The main characteristics of coastal areas are longshore currents supplied with river alluvium and coastal abrasion material. The volume of sedimentary material produced by abrasion amounts to 19-25% of the sediment input of the largest rivers of the Black Sea catchment area, such as the Danube, Dnieper, Don, Kuban and Inguri rivers.

The amount of sediments discharged to the sea at various coastal sections, as a result of abrasion process, is 27.4 10^6 m^3/yr. The underwater abrasion provides about 29 10^6 m^3/yr, 9.4 10^6 m^3/year including the beach-forming fraction (Shuisky, 1981).

In the Georgian coastal zone, approximately 17% of river alluvium (1.95 mln tons/yr) are involved in longshore movement and beach formation (Jaoshvili, 1986).

At 10-40 m water depths of the Caucasian shelf area, sediment fluxes vary from 0.19 to 10.27 mg/cm^2/day (average = 1.44) 3-5 m above the sea floor (Shimkus, 1993) (Table 7).

TABLE 7. Fluxes (mg/cm^2/day) of suspended matter (1989-1992 yr.yr.) in bottom waters (3-5 m over sea floor) of the Black Sea near Caucasus shallow water area (Shimkus, 1993; Shimkus and Komarov, 1996).

Water area	Water depth, m	Seasons	Fluxes	
			1	2
Anapa	14.0	S-A	1.23	1.23
Yu. Ozereyevka	25.0 40.0	SP,S,A,W S	0.09-3.82 0.13	1.5 0.13
Myskhako	39.0	S,A	1.08	0.90-1.26
Novorossiysk Bay (mouth)	19.5	SP,S,A,W	0.86	0,02-2.43
Blue Bay	10	SP,S,A	0.85	0.21-1.19
Gelendzhik Bay	8-11	SP,S,A,W	2.15	0.13-9.94
Opposite Gelendzhik	40	S,A	0.96	0.19-1.72
Idokopas	25 40	SP,S,A,W S,A	0.24-7.94 0.14-1.66	3.56 0.90
Archipo-Osipovka	26	S-A	1.66	1.66
Krinitza	25 40	S,A,W S	0.53-6.56 0.36	3.53 0.36
Khosta	25	S-A	1.43	1.43
Sochi	40	S	1.07	1.07
Psou	38	S,A	6.81-10.29	8.55

SP - spring, S - summer, A - autumn, W - winter; Fluxes: 1 - range of values, 2 - mean value.

They are characterized by significant spatial and temporal variations (Shimkus, 1993). High and maximum values are observed near the mouth areas of the open sea and in some sheltered parts of Gelendzhik Bay. At 20-25 m deep, these values are several times higher than at 38-40 m. Sediment fluxes tend to be still higher in spring and autumn, and less in summer and winter, though the difference is not prominent everywhere. This is due to the fact that small rivers with sharp fluctuations of a solid runoff depending on a synoptic situation supply sedimentary material from a drainage area. In rainy periods, which may occur in any season, the river runoff increases significantly. Similarly abrupt decreases occur during the intervals between rains. This causes a high variability of suspended matter concentrations in rivers. Besides the increase in the solid runoff of shallow rivers, rainy periods are characterized by supply of large masses of sedimentary matter by storm streams. In such rivers a direct dependence between the amount of atmospheric precipitation and the value of suspended material fluxes are observed. This is especially typical for the Gelendzhik Bay where precipitation rates vary both between and within the seasons.

Suspended material fluxes measured at testing sites near the bottom (0.7 m above the sea floor) vary markedly over short distances and the average of mean values at different testing sites range from 1.51 to 53.12 mg/cm^2/day (Shimkus, 1993).

The variations of values of the flux of suspended matter at different levels above the sea floor depend, not only on irregular sediment supply from drainage area, but also on the heterogeneity of the hydrodynamic field in general, and water mass and suspension transport by vortices in particular. The seasonal study of suspended solids in the Near Caucasian Sea zone during 1989-1991 revealed funnel-shaped lenses of high concentrations in the water column. Their formation is caused by anticyclonic vortices facilitating the penetration of suspended matter to the depth; in some cases the bottom of these «funnels» reach the sea floor (Shimkus, 1993). Thus, the flux of suspended matter near the bottom will increase along the routes of anticyclonic vortices, while they are lower in the adjoining areas.

The studied area near bottom suspension confirms the presence of silt, according to the Folk's classification and mainly silt-pelite and fine silt fraction with minor Pelitic silt according to the P.L.Bezrukov and A.P.Lisitzin's classification.

The percentage of pelitic fraction (<0.01 mm) determined in 83 samples varies from 48.76 to 80.40% (59.54% in the average) (Shimkus, 1993). Grain size of the suspension varies both temporarily and spatially. In some areas, the suspension is generally poor in subcolloidal fractions. An example is the area off the Psou river mouth (about 40 m depth) where they vary between 0.0 and 7.53%. A similar picture has been observed at similar depths off Gelendzhik in summer and autumn. In both cases, a significant increase of fine silt percentage was traced. The spatial heterogeneity of the grain size composition is likely the result of grain-size sorting of sedimentary material by eddy currents with different velocities.

Closer to the bottom (0.7 m above the sea floor), the grain size composition of suspended matter differs from the latter at 3-5 m level. This is confirmed by the data obtained at 6 testing sites at a depth interval of 14.5-20 m in the upper shelf between Novorossiysk and Adler . In three testing sites poorly sorted sandy-silty sediments with different portion of pelitic material is predominant. In the other three opposite Yuzhnaya Ozereyevka, Shakhe and Mzimta River mouths, moderately sorted silts and fine silts are accumulated at 19-20 m deep. In different points of the testing sites, the grain size composition of the suspension is heterogeneous. Sand and silt contents are especially fluctuant. This is due to the high variability of hydrodynamics within the testing sites. In some points of the Shakhe site, the sedimentation was approaching zero, while in other places the sediment accumulation was rather intensive. In the Adler testing site the area of bottom erosion alternated with those of zero accumulation. Suspension flows are of one kind and lower in the areas where the bottom erosion is developed, compared with the areas where sediment accumulation is predominant.

Bottom sediments are represented by sands and sandy-silts, occasionally by fine silts and muds in the areas of study of the suspended matter. The data obtained indicate a great loss of suspended subcolloidal, pelitic and, to some extent, silty material when approaching the sea floors. Due to high velocities of currents, the fine material is transported from the studied regions. The only exception is the sheltered corners of the Gelendzhik Bay, where a short-term deposition of significant amounts of organially rich, silty-pelitic muds occurs.

The near-bottom suspension is poor in carbonate material, especially opposite to the river mouths. The average content of carbonates is 30.17%, varying from 5.35 to 46.56% (Shimkus, 1993). At 8-20 m deep, the carbonate content in suspension is generally higher than at 40 m (5.35-20.12% of CaCO3). This is probably due to re-suspension of shelly material from the bottom. The carbonate content increases noticeably in some areas of the Gelendzhik and Novorossiysk Bays, which are less than 20 m deep.

The near-bottom suspension is enriched in organic matter (C_{org} = 1.20-5.49%, Average C_{org} =2.92%). High and maximum contents of organic matter are observed in the corners of the Gelendzhik Bay and in the wide throat of the Novorossiysk Bay and the adjacent area (Shimkus, 1993). Bottom sediments are considerably poorer in organic matter than the suspension itself. Thus, a major portion of organic matter does not reach the bottom sediments of the area near to the shore.

Sediment fluxes on the sea bottom are calculated using data of modern rates of accumulation of sedimentary material (Shimkus and Komarov, 1996); they are approximately 20-30 times less than the near bottom ones. This indicates that only less than 10% of sedimentary material of the near bottom waters is accumulating on the shelf, and that the rest is transported to the deep basin.

Deep-sea basin

Vertical fluxes of sediments measured by sediment traps -deployed at 250 m and 1200 m deep in the water column in the southwestern Black Sea- indicate sharp seasonal cyclic total values, lithogenic and non-lithogenic (biogenic carbonates, biogenic silica, organic carbon) fractions (Honjo et al., 1987). The total flux is usually higher at 250-m deep compared to 1200-m. The same picture is revealed as regards lithogenic fraction. The maximum of total flux is in winter 485 mg/m^2/day and 150 mg/m^2/day at 250 m and 1200 m deep, respectively. The lithogenic fraction in this season shows values around 360 and 70 mg/m^2/day. The largest difference occurs in the spring season. The differences in the total sediment flux and the lithogenic sediment flux between the two levels indicate indicate a significant lateral transportation of sedimentary material in the studied area. The estimated speed of particle-sinking varied between 65 m/day in summer and fall, and 125 m/day in winter and spring. According to sediment trap studies in the southwestern part of the Black Sea, particles of radionuclides penetrated to the depth of 1071 m after two weeks following the Chernobyl accident. Taking into account that the settling speed of suspended matter in the anoxic water column between 250 m and 1200 m deep during the winter-spring period is around 125 m/day (Honjo et al., 1987), the settling time to the depth of 1000 m is about 7.6 days and the delay of settling particles at the pycnocline interface may be around 3 days.

Vertical fluxes of terrigenous matter show a wide range of variations depending on the seasonal fluctuations of river discharge. The settling rates of particles increase during peaks of biological productivity, i.e. periods of mass pellet production (spring, summer, autumn). A considerable portion of dispersed terrigenous matter is incorporated into pellets as a result of biofiltration (Tambiev, 1987).

The size of micropellets produced by small zooplankton, which represent up to 40-50% of the total mass, is between 16 and 200 μm and they are composed up to 60-80% of coccoliths or their fragments, lithogenic particles (37-42,5%) and organic matter (4-15%) (Tambiev, 1987).

The settling speed of fecal micro pellets or «marine snow» flocs goes from 50 to 100 m/day, whereas the rate of large pellets may exceed 1000 m/day. According to my estimations based on sedimentation rates in the upper Holocene, the total fluxes of sediments on the sea floor are 3-6 times higher than those observed at 1200-m deep. This suggests that it is not the vertical settling, but the horizontal near bottom transport of sedimentary material which is more important in this case.

Near bottom currents are studied only along the Georgian submarine canyons (Jaoshvili, 1986). About 9.75 10^6 m^3/y of sediments (83% of the total river discharge) moved along canyons to the deep-sea basin, mainly to the continental rise. This is confirmed by the presence of turbidities in the sediment cores collected in the bottom of the Caucasian submarine canyons (Trimonis and Shimkus, 1970) as well as in the deep sea fan sediments (Ivanov et al., 1986). It is quite probable that a similar picture will be observed on the Turkish side of the basin, if one considers the analogy between the regime and the evolution of the erosion process. The fluxes of silty-pelitic, but also of pebble-gravel material in te river, coming from the Turkish watershed to the deep basin, are traced by finding this material on the bottom of submarine canyons at more than 1500 m deep (Zhigunov and Shimkus, 1984).

Maximum accumulation rates of sediments are characteristic of the Anatolian and Caucasian continental rises, where modern fans of terrigenous matter are developed (Crusius and Anderson, 1993; Hay, 1988; Shimkus et al., 1975) (Fig 1). They are more than ten times the rates observed in the central deep sea, underlying the main cyclonic gyres where biogenic sedimentation with coccolithic oozes and high organic carbon prevails (Fig. 1).

The rate of sediment accumulation calculated on the deep sea floor is twice to six times higher than those measured by the sediment trap deployed at 1200 m deep in the southwestern Black Sea (20-60 g/cm^2/k.yr vs. 10.95 g/cm^2/k.yr). According to the Pb-210 age measurements, the coccolithic ooze deposition is taking place at about 5-2 g/cm^2/k.yr on the Black Sea floor (Crusius and Anderson, 1993).

Pollutants

Shallow water area

Water column.

An intensive accumulation of sedimentary material and pollutants takes place on the river/sea barrier area. In the estuary of the Kuban River, nearly 95.8% of the total suspended matter settles down from the surface layer to the mixing zone of the river and/or sea waters where the rate of salinity increases from 0 to 4‰. The concentration of suspended matter in this area decreases more that 20 times. The waters, with a salinity from 4 up to 12 ‰, show only a slight reduction of turbidity, with a minimum observed with a 12 ‰ salinity (Demina, 1982).

The loss of a considerable part of particles of pollutants results in the dissolution of these particles in the estuaries. This process is very intensive for some HM, such as Cu and Zn (Demina, 1982). Unfortunately, the behaviour of different pollutants in the estuaries of other Caucasian rivers has not been studied.

In the bottom waters of the Caucasian shelf area, fluxes of different HM particles are variable (Table 8,9).

TABLE 8. A content of HM (ppm) in suspended matter from near bottom waters (3-5 m above sea floor); of the Caucasian zone of the Black Sea (1989-1992) [Shimkus et al., 1994, 1996].

Area	Depth, m	Cu		Zn		Pb		Cd	
		a	b	a	b	A	b	a	b
Gelendzhik Bay	8-11	16-167	41	30-1063	161	25-130	51	1.4-10	4
Novorossiysk Bay	19.5	20-213	51	70-486	160	25-138	64	0.6-10	5
Yu. Ozereyevka	25	10-128	38	43-1100	281	30-250	67	2.0-12.6	5
Idokopas	25-40	10-36	21	20-362	104	5-70	28	2.4-10	3
Krinitza	25-40	8-30	24	53-150	185	20-40	24	-	10
Psou	38	32-76	47	78-350	185	20-71	41	-	10
Sochi	40	26-50	38	99-750	329	20-35	27	1.0-17.4	12

A-range of content; b-mean value.

TABLE 9. Fluxes of particulate heavy metals in the near bottom waters (3-5 m above sea bed) of the Black Sea Near Caucasus shallow water area (1989-1992.) (Shimkus et al., 1996).

Area Water area	water depth, m	Seasons	ug/cm²/day												mg/cm²/day	
			Cu		Zn		Pb		Cd		Ni				Fe	Mn n x 10^{-2}
			1	2	1	2	1	2	1	2	1	2	1	2	1	2
Anapa	14	S-A	-	3.0	-	11.0	-	5.0	-	0.2	-	4.0	-	2.0	-	5.3
Yu. Ozereyevka	25 40	SP,S,A, W S	0.2-9 -	3.0 0.7	1-30 -	13.0 20.0	0.5-14 -	7.0 2.0	0.1- 1.1 -	0.5 0.1	0.5-13 -	6.2 1.0	0.1-3.7 -	1.35 0.22	0.5-11.8 -	5.5 0.8
Myskhako	39	S,A	-	1.0	9-15	12.0	1-3	2.0	-	0.2	1-2	1.5	-	0.9	-	2.1
Novorossiysk Bay	19.5	S,A	0.8-3	1.9	2-11	6.5	2-6	40	0.1- 0.3	0.2	-	2.0	0.1-0.81	0.5	2.2-4.3	3.3
Blue Bay	10	A,W	3-4	3.5	6-15	10.5	3-6	4.5	-	0.4	3-5	4.0	-	1.5	-	7.8
Gelendzhik Bay	8-11	SP,S,A, W	2-21	6.9	8-59	23.5	4-75	17.4	0.3- 6.0	1.6	3-35	12.2	0.9-10.7	4.3	4.4-40.6	18
Opposite Gelendzhik	40	S,A	0.6-4	2.3	8-66	37.0	2-7	4.5	-	-	0.6-5	2.8	-	2.8	-	4.6
Idokopas	25 40	SP,S,A, W S-A	0.4-8.7 -	5.8 4.0	5-48 -	24.8 29.0	1-28 -	13.8 4.0	0.1- 2.5 -	1.1 -	1-11 -	6.0 5.0	0.5-3.8 -	2.2 2.5	2.1-39.2 -	20.7 2.1
Archipo-Osipovka	25	S-A	-	6.0	-	17.0	-	8.0	-	0.2	-	7.0	-	2.7	-	5.5
Krinitza	25	S,A,W	1-14	7.0	4-39	27.0	1-26	13.0	0.2- 2.0	1.0	1-8	5.0	2.6-11.0	6.8	12.3-51.2	31.9
Khosta	25	S-A	-	5.0	-	20.0	-	23.0	-	0.3	-	6.0	-	2.7	-	5.7
Sochi	40	S,A	5-12	8.0	60-154	107.0	6-16	11.0	-	1.9	6-28	17.0	-	7.4	-	12.1
Psou	38	S,A	30-51	40.0	111-209	160.0	24-51	38.0	-	-	22-61	42.0	-	17.0	-	46.3

SP - spring, S - summer, A - autumn, W - winter, 1 - range of contents, 2 - mean value.

The highest values are typical with Zn and the lowest ones with Cd (Table 4). In the Sochi water area , the maximum fluxes have been observed near the Psou river mouth, not only for Zn, but also for Cu, Pb, Ni and Fe. High fluxes of Zn, Fe and Mn were also observed in the protected areas of the Gelendzhik Bay. In some seasons, relatively elevated values of Cd fluxes were observed locally, both in the Sochi and other water areas (Krinitsa, Idokopas).

The fluxes of Zn in the Sochi area are particularly high in autumn, whereas Cu and Pb fluxes are partly high in autumn or summer. The autumn and winter maxima are typical for the shelf area between Novorossiysk and Arkhipo-Osipovka, but the semi/enclosed Gelendzhik Bay is characterized by a summer maximum for all heavy metals studied (Shimkus et al., 1994,1996).

Fluxes of OP and PAH in marine suspended matter reach their maximum values off the Sochi-Tuapse area, near the mouth of the most polluted rivers, such as Tuapse, Mzimta and Psou, and in the Novorossiysk and Gelendzhik Bays where the contamination is related mainly to the existence of oil ports (Table 10, 11).

Spatial distribution of HM as well as OP, PAH and PS has a strongly pronounced lens shape and a spotty character (Figs. 2-3 and 5-10). The origin of a number of tongues stretching offshore, present high concentrations of different pollutants associated with the supply of Caucasian rivers of various sizes. Important polluted water lenses occur at a definite distance from the river mouths, due to vortex transport of pollutants into- surface waters.

An approximate coincidence of the maximum concentration fields is observed for Zn, Pb and OP, whereas the maximum PS and Hg contents are observed in different locations.

TABLE 10. Contents of OP and PAH in suspended matter from near bottom waters (3-5 m above sea floor) of the Caucasian shelf area (Shimkus and Komarov, 1996).

Water area	Water depth, m	Years	Seasons	OP mg/kg	3,4 - benzopyrene ng/kg	1.12-benzperilene ng/kg
Gelendzhik Bay	8.0-11.0	1990-1992	S,A,W,SP	0.6-83.8 42.6	0.0-9.90 4.40	0.0-0.54 0.28
Novorossiysk Bay	19.5	1990-1992	S,A,W	15.3-389.3 154.4	0.0-16.90 5.30	0.0-2.30 1.12
Blue Bay	10.0	1991-1992	S,A,W,SP	0.9-78.6 29.5	0.0-0.24 0.08	0.0-0.05 0.02
Anapa	14.0	1992	S-A	3.2-42.5 20.0	0.0-0.60 0.25	0.17-0.26 0.21
Yu-Ozereyevka	25.0	1990-1991	S,A,W,SP	18.9-37.7 29.3	0.0-1.60 0.62	0.0-0.17 0.11
Myskhako	39.0	1991	S,A	109.2-467.4 288.2	3.80-17.50 10.65	0.56-2.40 1.48
Idokopas	25.0	1990-1991	S,A,W,SP	4.80-33.6 14.7	0.0-6.70 1.76	0.0-0.32 0.13
Archipo-Osipovka	25.0	1992	S-A	5.2-13.9 9.6	0.0-0.34 0.17	0.5-0.5 0.5
Krinitza-1	25.0	1990-1991	S,A,W	5.7-45.5 16.7	0.0-0.93 0.78	0.0-0.31 0.13
Krinitza-2	40.0	1991	S	30.0	0.0	0.0
Khosta	25.0	1991	S-A	8.9-22.7 15.8	0.0-0.38 0.19	0.06-0.14 0.10
Sochi	40.0	1991	S,A,W	21.3-474.0 221.7	1.2-12.4 5.42	0.0-1.79 0.65
Psou	38.0	1991	S,A	8.0-16.0 12.0	0.31-0.49 0.40	0.09-0.11 0.10

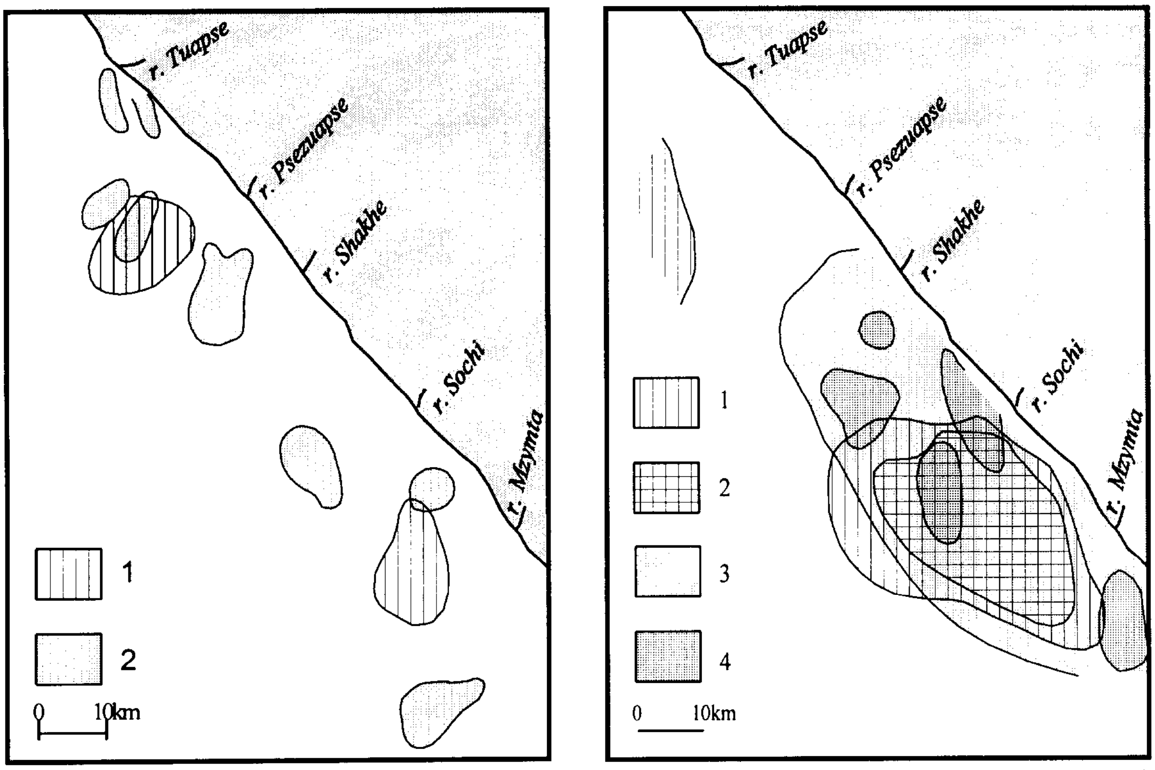

FIGURE 1-2. Maximum concentration of Pb in surface waters (1) and in recent bottom sediments (2) of the Tuapse - Sochi area (data from Shimkus et al., 1996).
1 – >3 μg/l; 2 – >40 ppm.

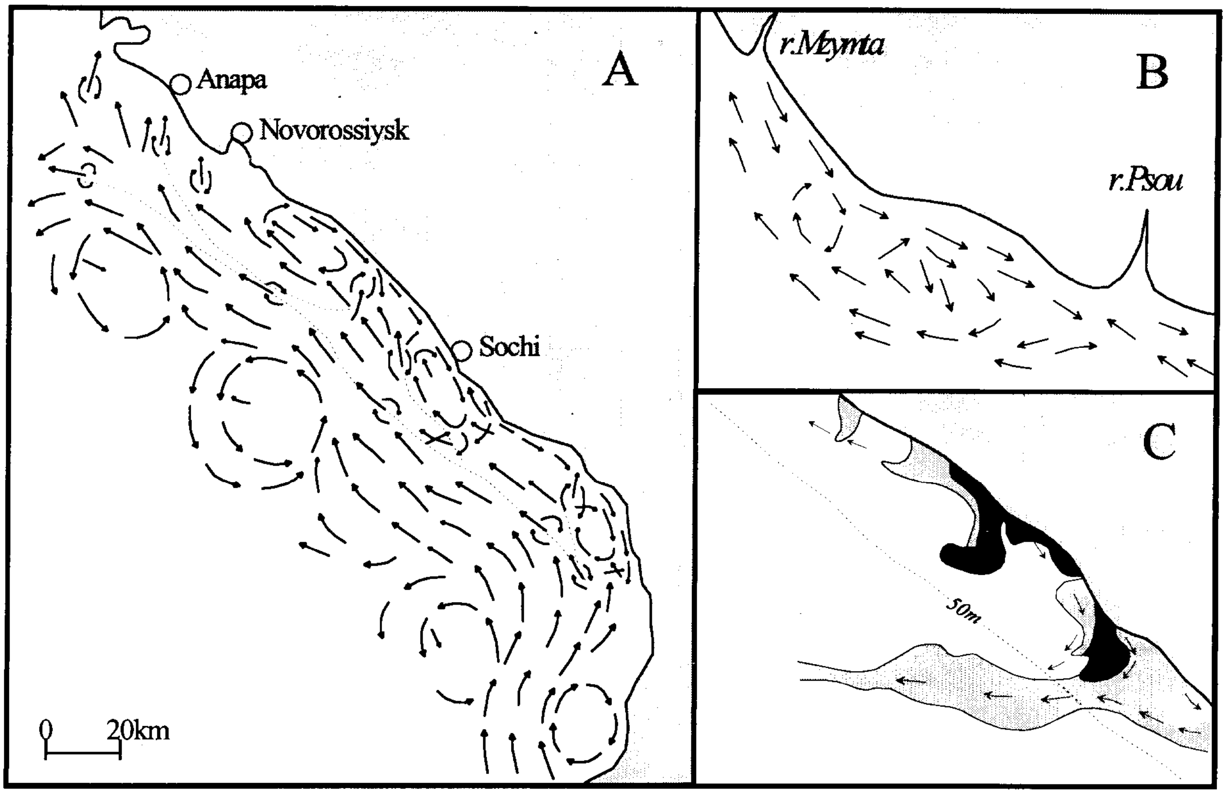

FIGURE 3-5. Cyclonic and anticyclonic vortices (A,B) and trend of reverse material transportation near the river mouths (C) on satellite data (Yeletskiy et al., 1992). Transition from the black to dotted areas on C designates decreasing concentrations of reverie suspended matter.

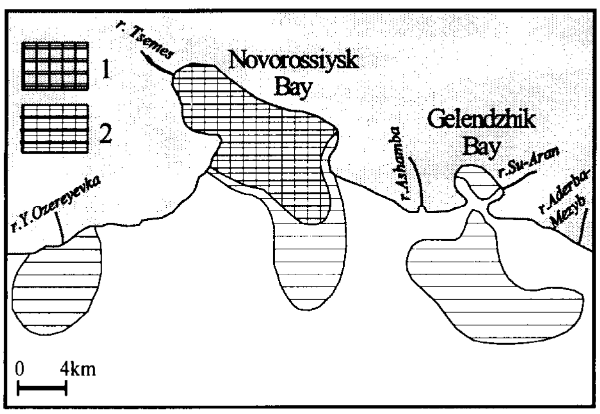

FIGURE 6

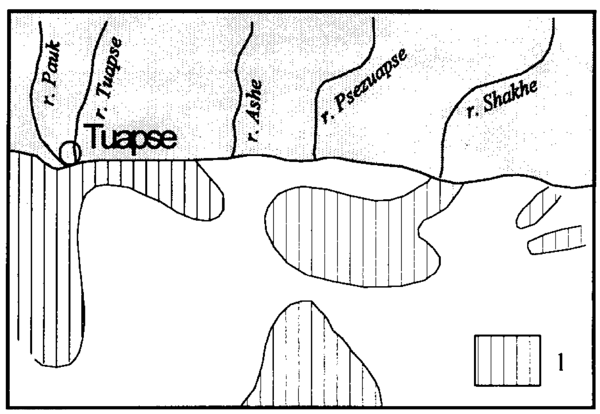

FIGURE 7

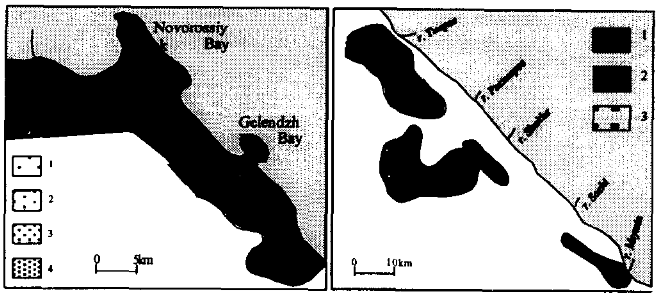

FIGURE 8

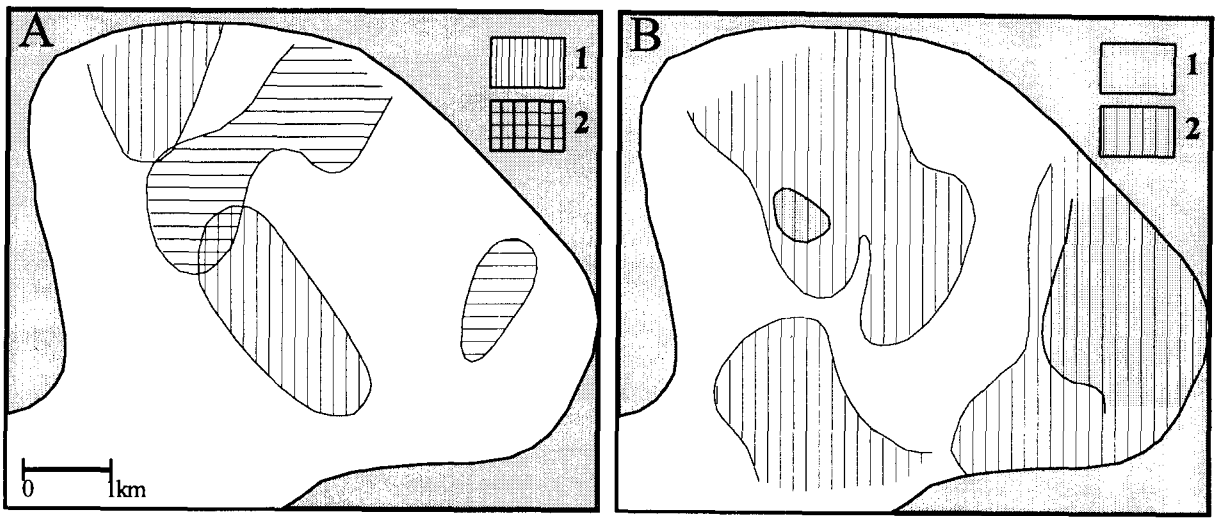

FIGURE 9. Maximum content of 1,12 - Benzperylene (A) and bituminous material (B) in recent bottomsediments of the Gelendzhik Bay (data derived from (Pikovsky and Komarov, 1996).
A. (>8 ng/g): 1– winter; 2 – summer.
B. 1 – hexane extracts (>0.01 %); 2 – chloroforming extracts (>0.06 %).

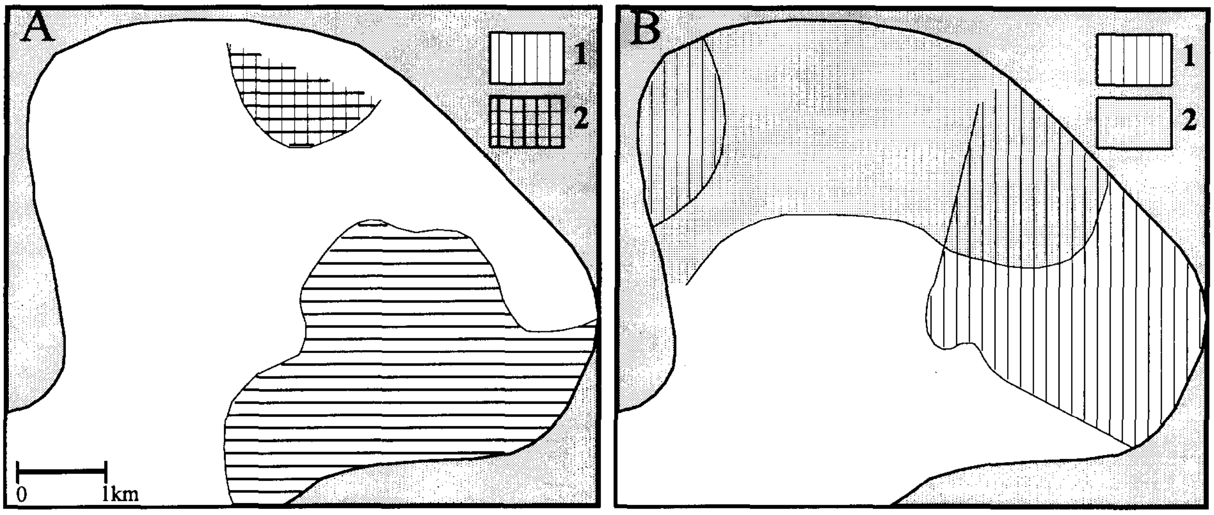

FIGURE 10. Maximum concentration (μg/l) of Pb (A) and Zn (B) in surface waters in summer 1988 (1) and 1991 (2) in the Gelendzhik Bay (data from Komarov and Shimkus, 1996; Shimkus et al., 1996). A. 1 – >4, 2 – 60-150; B. 1 – 40-50, 2 – 160-250.

Bottom sediments.

Sediments polluted with HM are located, as a rule, at some distance from the river mouth. This is typical for Cu and Zn. Only fields of elevated Pb and Hg concentrations are close to deltas (Figs. 2, 3). Some large fields denting the space between river mouths are observed in the Sochi-Tuapse region. Isolated fields are most likely the result of a rapid accumulation of sedimentary material under anticyclonic eddy influence in the coastal zone. In the bottom sediments concentrations of Cu, Zn and Pb progressively increases from sandy-silty to pelitic fractions, whereas Cd contents is several times higher in sandy material than in the finer fractions. In near bottom waters suspension material consists mainly of coarse silt, which is likely to be fecal pellets formed by sediment biofiltration of benthic mollusks. (Table 12,13).

Spotty distribution of high concentrations in bottom sediments is characteristic for hm, op, pah and ps (fig 2,3,5,6,7,8,9,10). Such a distribution is a direct consequence of the transport and accumulation by vortices developed along the near-caucasus zone (fig. 4). The picture is complicated by action of near bottom currents (Titov, 1992; Yeletskiy et al., 1992).

TABLE 11. Near bottom fluxes at (3-5 m above sea floor) of particulate oil products (OP) and polycyclic aromatic hydrocarbons (PAH) in the northwestern Caucasus shallow water zone (Shimkus and Komarov, 1996).

Water area	Water depth, m	Years	Seasons	$ng/cm^2/day$	$ng/cm^2/day \times 10^{-4}$	
				OP	BP	Bpr
Gelendzhik Bay	8.0-11.0	1990-1992	S,A,W,SP	0.06-20.82 7.02	0.0-7.530 4.305	0.051-0.848 0.425
Novorossiysk	19.5	1990-1992	S,A,W	1.22-15.26 8.03	0.0-1.166 0.532	0.0-2.309 0.802
Blue Bay	10.0	1991-1992	S,A,W,SP	0.05-1.97 1.03	0.0-0.286 0.095	0.0-0.005 0.0025
Anapa	14.0	1992	S-A	0.39-5.23 2.46	0.0-0.738 0.312	0.209-0.320 0.254
Yu. Ozereyevka	25.0	1990-1991	S,A,W,SP	0.70-11.12 5.67	0.0-4.720 1.588	0.0-0.420 0.1435
Myzkhako	39.0	1991	S,A	9.83-58.89 34.36	3.42-22.05 12.74	0.504-3.024 1.764
Idokopas	25.0	1990-1991	S,A,W,SP	0.81-5.82 3.21	0.0-1.608 0.728	0.0-0.293 0.142
Archipo-sipovka	25.0	1992	S-A	0.86-2.31 1.59	0.0-0.564 0.282	0.083-0.083 0.083
Krinitza-1	25.0	1990-1991	S,O,W	0.31-7.09 4.24	0.0-5.069 2.118	0.0-0.484 0.394
Krinitza-2	40.0	1991	S	1.08	0.0	0.0
Khosta	25.0	1991	S-A	1.27-3.25 2.26	0.0-0.777 0.389	0.096-0.20 0.143
Sochi	40.0	1991	S,A	2.28-46.99 24.63	1.28-3.79 2.537	-
Psou	38.0	1991	S,A	8.23-10.89 9.56	2.11-5.04 3.58	0.613-1.132 0.873

Comments: BP - 3,4 benzpyrene; Bpr - 1.12 - benzperylene, S - summer, A - autumn, W - winter, Sp - spring; figures: numerator - range of values, denominator - average.

TABLE 12. A mean content of HM in granulometric fractions of suspended matter from near bottom waters (3-5 m above sea floor) of the Caucasian shelf (Novorossiysk - Archipo-Osipovka area) (Shimkus et al., 1996).

Factions, mm	ppm						
	Cu	Zn	Pb	Cd	Ni	Fe	Mn
0.1-0.05	50	105	92	2.3	21	1.12	0.039
0.05-0.01	61	189	113	4.4	39	-	-
<0.01	-	89	198	13.8	-	-	-

TABLE 13. A mean content of HM in granulometric fractions of the Caucasian shelf bottom sediments (Sochi - Tuapse area) (Shimkus et al., 1996).

Factions, mm	ppm						
	Cu	Zn	Pb	Cd	Ni	Fe	Mn
>0.1	37	48	58	3.0	28	0.82	27
0.1-0.05	60	81	52	1.3	35	2.27	69
0.05-0.01	73	120	39	1.3	45	2.71	78
<0.01	101	141	76	1.4	54	3.13	78

It should be emphasized that there is no exact coincidence of the fields of maximum concentrations of different pollutants in the surface and bottom water layers, as well as in the bottom sediments. Instead a more or less spatial shifting is observed between the different pollutant patterns. This suggests that the transport of pollutants is deposited on the seafloor by currents of different directions. In the coastal zone they are sharply reduced in the near bottom layer because of strong bottom currents. Locally in some areas of the middle and outer shelf where currents are relatively weak, pollutant fluxes are sufficiently high on the bottom to produce anomalous high concentrations of different pollutants in the sediments. In the sheltered parts of the semi-closed bays where bottom currents are weak a similar situation prevails.

Deep sea basin

Water column

Strong pycnocline separating oxygenated and reducing environments has hardly affected the distribution of pollutants. However, a marked enrichment is observed in particulate manganese and iron above the oxygen-zero (Emelyanov et al., 1975, 1976; Haraldson and Westerlund, 1991) because of the precipitation of MnO_2 and ferric hydroxide from the upward transport of dissolved Mn^{2+} and Fe^{2+} in the anoxic water below. A calculated upward flux for the manganese is 675 mg/m^2/year and for iron 43.3 mg/m^2/year.

Once formed, the particles of MnO_2 and ferric hydroxide sink and dissolve again in the reducing anoxic water column. Particulate cobalt, manganese and iron all show a distinct maximum at the oxic/anoxic interface. For the elements with a strong tendency to form sulfide complexes, such as Cd, Cu, Pb and Zn, there is a clear decrease starting at the oxic/anoxic interface region. Their maximal is found in the center of oxic/anoxic interface, where it could possibly have been generated by biological activity. Ni, Co, Fe, Mn, on the other hand have their minimum here.

Large volumes of pollutants are carried away from the shelf by bottom currents and turbidity flows along submarine canyons having their apices cutting shelf near the mouths of great Caucasian and Turkish rivers. Such canyons as Bzyb, Kodori, Inguri, Rioni, Çoruh, Kızılırmak are highly fed not only by pollutants incorporated in riverine suspension and alluvium, but also in sedimentary matter transported by long shore fluxes.

Bottom sediment

The strips of deep sea sediments enriched in HM (Mitropolskiy et al., 1982) are coincided to the drainage areas where the rocks enriched in these elements are widespread and mining industry is developed (Yücesoy and Ergin, 1992). Some layers of silty - pelitic muds embedded in the modern turbidity sequences are very enriched in Pb, Zn, Ni, Cu, Cr and Mn on the southwestern and southern continental rise of the Black Sea basin (Baykurt et al., 1982), with Zn- up to 693 ppm, Cu-up to 550 ppm, Cr up to 578-1090 ppm and Ni up to 672 ppm. Most probably the high metal values have a technogenic source. Anthropogenic origin of the anomalously high concentrations of Mn, Cr, Zn, Pb is confirmed by unusual Fe/Mn, Ti/Cr, Ni/Cr and Pb/Zn values that are atypical of the natural source materials.

Strong supply of anthropogenic Zn, Cr and Cu is provided from the northwestern and western drainage areas; Pb, Zn, Cr and Ni from the Pontides and coastal zone of Turkey, and Mn from Georgia. The most intensive accumulation of the pollutants takes place on the continental rise of the deep Black Sea basin where modern sediment fans are being developed. Sediment accumulation rates in upper Holocene are the highest in these parts of the basin (Fig. 1).

A weak accumulation of the pollutants is proposed for the vast bottom areas underlying the cyclonic gyres of the surface waters which are characterized by low sediment accumulation rates (Hay, 1988; Hay et al., 1991; Hay and Honjo, 1981; 1989; Shimkus et al., 1973, 1975; Shimkus and Komarov, 1996).

BUDGET

Previous data (Hay and Honjo, 1989; Emelyanov et al.,1975, 1976; Shimkus and Trimonis, 1974) characterize separate balance parts both of sedimentary material and heavy metals. For instance, it was established by Emelyanov (1976) that absolute masses of Fe, Al, Ti and Mn in the water column exceed their annual river input 4.5, 1.4, 2.0 and 1.7 times, respectively. There is not an n easy explanation of this discrepancy. Accumulation modules of the elements in the deep Black Sea basin are 5-20 times higher than those in the shallow waters (Table 14).

Table 14. Mean modules of accumulation of Fe, Al, Ti, Mn on the Black Sea bottom (Emelyanov et al., 1976).

Region	Area, km^2	$t/km^2/yr$			
		Fe	Al	Ti	Mn
Shallow water (0-200 m)	112852	7.72	5.82	0.21	0.18
Deep water (200-2200 m)	307473	85.30	57.40	3.04	1.02

Maximum absolute masses of Fe, Al, Ti, Mn in the water column gravitate to the Turkish and the Caucasian continental rises where the highest rates of their accumulation on the sea bottom are occured [27]. An attempt to calculate balance of organic materials has been made by V.G.Datsko (Table 15).

TABLE 15. Approximate balance of organic material in Black Sea (recalculated on water free basis) (after Datsko, Shimkus and Trimonis, 1974).

Inflow	$n \cdot 10^3$tons	Deposition	$n \cdot 10^3$tons
Production of phytoplankton	100,000	Deposition on floor	12,000
Production of macrofites	2,400	Undergoes mineralization	95,885
Supply from watershed and during water exchange with the seas	9,000	Loss during water exchange with other seas	3,500
		Removed by man	15
Total	111,400	Total	111,400

Exact budget calculations for the sedimentary material, its main components, and of the various pollutants have not been made despite existence of reliable data on the water balance (Altman, 1991). The reason for this is the insufficient information on the input of the dissolved and particulate materials from the catchment area. In particular, reliable data on the amounts of fluxes of various materials in the water column, their rates of accumulation on the Sea floor and in the sediments are lacking. Moreover, data on the exchange of most materials with the Sea of Marmara through the Bosphorus Strait are not yet available.

CONCLUSIONS

1. Although maximum supply of sedimentary material in multiannual series is received from the northwestern watershed, in some seasons and years the southern watershed also contributes significant amounts. This change in the supply is caused by a large and synchronous variation in the solid runoff of the northwestern and the Southern rivers, which is, in turn, controlled by natural climatic changes in the last fifty years and by increasing regulation of the river runoff.

2. Sedimentary flux studies in the water column using sedimentary traps in deep southwestern Black Sea revealed strongly pronounced seasonal fluctuations. These fluctuations are correlated with seasonal and annual oscillations of the river runoff from the southern and, in part, from the northwestern watersheds and with seasonal fluctuations of biological productivity.

3. Fluxes of sedimentary material in the near-bottom water layer in a shallow region (depth is 20-40 m) greatly exceed the rates of sediment accumulation on the sea floor, whereas an opposite picture is observed in a deep-water region. This indicates that considerable part of the sedimentary material is transported over the upper and partly the middle shelf zones and accumulates at elevated rates on the margins of the deep basin. This, in turn, indicates that the high sediment accumulation rates are mostly due to the near-bottom suspension fluxes but not to the vertical sediment fluxes.

4. Maximum supply of pollutants to the Black Sea is connected with the river runoff from the northwestern watershed; the role of other drainage areas in supply of pollutants is not presently well known. However, the geo-ecological monitoring results from the Near Caucasian zone of the Black Sea show that both small and medium size rivers may be a serious source of pollution in the near-shore zone, primarily in the water column and in the bottom sediments of the semi-closed bays. In the open basin maximum fluxes of pollutants are observed near the foot of the slope, where they are supplied by descending vertical and by near-bottom suspension fluxes.

5. The budget of sedimentary material and pollutants can not be estimated due to an evident lack of data on matter fluxes in the basin and on their exchange with the Sea of Marmara and the Sea of Azov. Some previous attempts to calculate the balance have been made on the basis of a very poor actual material, and can therefore, be regarded as only very tentative. The success in this direction can be achieved by obtaining new data on chemical and granulometric composition of the river runoff and aerosol materials and their fluxes, as well as on the matter exchange between with the adjacent basins though the straits.

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RIVER RUNOFF AND SEDIMENT DISCHARGES INTO THE BLACK SEA

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ABSTRACT

River sediments are very important in the processes of marine sedimentation and pollution. In spite of this importance, the issue has not been well studied before. The following work is the first to consider river runoff and sediments discharge into the Black Sea. Data obtained from more than 100 rivers were used in this study.

INTRODUCTION

The Black Sea basin covers an area (2.5 million km^2) of asymetric form and the river discharges into this basin are built up in various nature and climatic conditions. The total of this type of rivers, running to the Black Sea, is about 500, and they differ from one another by the size of their catchment areas and the degree of study. Their water mass fluctuates within large limits. The more significative maximum specific discharge takes place in the subtropical region of Adzhar (60-70 litre/sec - km^2), and the minimum in the northern and western areas of the sea (1-2 l/sec - km^2).

These rivers discharge into the sea a great amount of sediments that accumulate on coasts, deltas of large rivers and take part in the modern process of sedimentation in the deep parts of the Black Sea. Sediments originate in the land and their quality depends on the characteristics of the river basins and their transport capacity.

RIVER RUNOFF

Along the Caucasus coast, numerous small and middle-size rivers discharge themselves into the sea. Their catchment areas increase southward by moving away from the Main watershed range from the sea. For defining the river flow into the sea, only rivers with watershed areas greater than 50 km^2 have been taken into account. The water input by the flow of small rivers is negligible and irregular; it influences only locally and irregularly the "within river - mouth offshore". The flow of the Caucasus rivers has been calculated on the basis of data of regular river hydrometrical observation (Resources of surface water of the USSR, 1974; State Water cadastr, 1987) and using a general method of flow calculation in mountainous countries, based on determination of the relation between flow and altitude in the area considered. Data from former studies were also used (Dzashvili and Papashvili, 1993; Hydrology of river Bzibi, 1981; Joashvili, 1984, 1986, 1989, 1991, 1995; Khalatian, 1977; Khmaladze, 1978; Kochetov, 1991; Mandich, 1965).

In the North-eastern part of the sea located in Russia, the total number of river runoff (with minor rivers) is 6.5 km^3 a year. The annual runoff of the majority of rivers is less than 0.15 km^3. The largest river is the Mzimta, that discharges more than 1.5 km^3 of water into the sea are shown in Table 1.

In the eastern part of the basin, the large Georgian rivers discharge into the sea an important volume of fresh water. The total amount of water input here is 45.5 km^3 annually. Bzibi (3.79 km^3), Kodori (4.17 km^3), Eristskali channel (3.15 km^3), where Inguri's runoff is transferred after regulation, Rioni (13.38 km^3) and Chorokhi (8.43 km^3) discharge the largest quantity of water into the sea (Table 2). Data on the Georgian rivers are obtained from various flow, apart from regular hydrometric observations (Hydrology of river Bzibi, 1981; Khalatian, 1977; Khmaladze, 1978; Mandich, 1965) and my own work.

There are less hydrological observations on the rivers of Turkey than on other rivers, which explains why the flow was calculated here on the basis of literature source (Algan et al., 1997; Dedkov and Mozjerin, 1984; Milliman and Syvitski, 1992; Reshetnikov, 1984), obtained by analogy and use of precipitation. The flow was determined for large rivers and interstream areas. It should be observed that the majority of rivers in Turkey is regulated, and that they are under anthropogenic pressure, which complicates the calculation. The total runoff discharge into the Black Sea in Turkey is 40.0 km^3 (apart from the Chorokhi and Veleka rivers). Half of this flow belongs to the large rivers: Yeþilýrmak, Kýzýlýrmak, Filyos and Sakarya. About one third of the runoff of the Black Sea basin of Turkey is formed in the subtropical region of the extreme Eastern part of the interstream area, from Chorokhi to Yeþilýrmak. This interstream area represents 24,000 km^2; it is equivalent to 10.4 % of the total catchment area of the Black Sea in Turkey (Table 3).

In the western part of the basin located in Bulgaria, small rivers discharge into the sea. Their total flow is 1.2 km^3. The largest of them are the Veleka and the Kamchia. They discharge into the sea 0.276 km^3 and 0.607 km^3 of water, respectively (Table 4) (Bulgarian Black Sea Coast, 1979; Dimitrov et al., 1997; Gergov and Veselinov, 1982).

In Romania, only temporary water streams discharge into the sea, except for the largest river of the Black Sea basin – the Danube - with a catchment area of 817,000 km^2, an expenditure of water in the river-mouth of 6,268 m^3/sec, and a specific runoff of 7.67 l/sec- km^2. The river discharge into the sea represents 198 km^3 of waters annually (Bondar and Blenda, 1997; Dedkov and Mozjerin, 1984; Gordeev, 1983; Mikhailov and Mikhailov, 1991; Milliman and Syvitski, 1992; Spatary, 1990).

In Ukraine, the large rivers (Dniester, Ingul, South Bug and Dnieper) discharge into the sea 65.8 km^3 of water annually. The only Dnieper pours 49.2 km^3 (Table 5) (Dedkov and Mozjerin, 1984; Milliman and Syvitski, 1992). The runoff of small rivers of Crimea is only 0.3 km^3 (Table 6) (Dedkov and Mozjerin, 1984).

To sum up, the total river discharge in the Black Sea represents 353.3 km^3 of water annually, a 75 % of which coming from the Northwestern part of the sea.

SEDIMENT DISCHARGE

Being the principal agent of land erosion, the rivers transport weathered rocks from the elevated areas to lower ones. The final accumulation of detritus ends in seas and oceans. During this process, part of the alluvium is accumulated in the coastal zone. The coastal zone acts as a filter for detritus discharging from the land to the ocean, which delays the terrigenous material for further treatment or long preservation and supplies it to the rest zones of the ocean (Longinov, 1973). In this process, the main role belongs to river-mouths, since the alluvial material is differentiated and sorted out in coastal (beach-forming) and marine (deep-water) materials. Thus, the river/sea mouth represents an important area for natural research.

The alluvium coming from the River enters the river-mouth as suspended load and bed load. Their mode of transfer depends on the grain-size of sediments. Usually, bottom sediments are coming form the coast (beaches forming). Coarse suspended load may also end up as coastal deposits, as it often happen in the case of mountain rivers. Sediments are divided into coastal and marine ones; usually, beach-forming sediments are coarser than 0.25 mm on the deeper pebble shores, and coarser than 0.1 mm on sandy shores (Dzaoshvili and Papashvili, 1993; Joashvili, 1984, 1986, 1991).

TABLE 1 . Rivers of the North - Eastern coast.

N	Rivers	Basin area, km^2	Basin average altitude, m	Water flow			Sediment load			Beach-forming sediments, 1000 m^3/yr.	Marine sediments, 1000 m^3/yr.
				M^3/sec	l/sec. km^2	Km^3/yr.	1000 t/yr.	1000 m^3/yr.	m^3/km^2 - - yr.		
1.	Sukko	89.2	180	0.69	7.7	0.022	12.3	6.83	76.6	3.0	3.83
2.	Diurso	53.7	190	0.45	8.4	0.014	1.32	0.77	14.3	0.5	0.27
3.	Ozereika	52.5	150	0.35	6.6	0.011	7.40	4.1	78.1	1.8	2.3
4.	Tsemes	82.6	130	0.51	6.2	0.016	11.30	6.3	76.3	2.0	4.3
5.	Mezib	194	200	3.86	19.9	0.122	67.2	37.3	192	13.5	23.8
6.	Jankhot	49.0	230	1.14	23.3	0.036	20.5	11.4	232	4.0	7.4
7.	Pshada	358	310	9.82	27.4	0.310	56.8	33.4	93.2	14.0	19.4
8.	Vulan	278	240	6.36	22.9	0.200	59.0	32.8	118	12.0	20.8
9.	Jubga	100	140	1.52	15.2	0.048	30.5	16.9	169	4.5	12.4
10.	Shapsukho	303	210	7.03	23.2	0.222	113.0	62.8	207	15.5	47.3
11.	Nechepsykho	225	150	4.59	20.4	0.145	87.7	48.7	216	12.5	36.2
12.	Tu	59.1	210	1.36	23.0	0.043	24.8	13.8	233	4.5	9.3
13.	Nebug	73.3	320	2.53	34.5	0.080	42.3	23.5	320	8.0	15.5
14.	Agoi	91.8	330	3.39	36.9	0.107	56.0	31.1	339	9.0	22.1
15.	Tuapse	352	335	12.8	36.3	0.404	110.7	65.0	184	17.0	48.0
16.	Shepsi	57.5	310	1.93	33.5	0.061	31.4	17.5	304	5.5	12.0
17.	Ashe	282	570	12.4	43.9	0.390	57.0	33.5	118	15.5	12.0
18.	Psezuapse	290	700	15.4	53.7	0.486	91.5	53.8	185	20.0	33.8
19.	Shakhe	553	890	36.8	66.5	1.161	211	124	224	45.0	79.0
20.	Dagomis	103	200	2.06	20.0	0.065	44.5	24.7	240	8.0	16.7
21.	Sochi	296	720	16.1	54.3	0.508	101	59.5	201	20.0	39.5
22.	Matsesta	67.5	306	2.28	33.8	0.072	31.3	17.4	258	6.0	11.4
23.	Khosta	93.5	410	4.90	52.4	0.155	31.5	18.5	197	8.0	10.5
24.	Cudepsta	87.1	347	3.39	38.9	0.107	38.2	21.2	243	6.0	15.2
25.	Mzimta	885	1309	49.5	55.9	1.562	258	158	376	60.0	98.0

TABLE 2. Rivers of the Eastern coast.

N	Rivers	Basin area, km²	Basin average altitude, m	Water flow			Sediment load			Beach - -forming sediments, 1000 $m^3/yr.$	Marine sediments, 1000 $m^3/yr.$
				m^3/sec	$l/sec. km^2$	$km^3/yr.$	1000 t/yr.	1000 $m^3/yr.$	m^3/km^2 - - yr.		
1.	Psou	421	1110	19.2	45.6	0.606	157.5	90.8	215	38.0	52.8
2.	Khashupse	200	1210	9.5	47.5	0.300	80.5	46.0	230	23.8	22.2
3.	Jove-Kvara	72	1520	6.11	84.8	0.193	53.7	30.7	426	15.3	15.4
4.	Bzibi	1510	1570	120	79.5	3.79	767.0	445.0	295	133.0	312.0
5.	Mchishta	169	720	7.71	45.6	0.243	20.2	11.7	69.2	2.2	9.5
6.	Khipsta5	166	1220	9.76	58.8	0.308	34.4	19.7	119	11.0	8.7
7.	Aapsta	243	670	10.8	44.4	0.341	37.7	21.6	88.8	9.5	12.1
8.	Gumista	576	1050	33.3	57.8	1.051	264.0	153.0	265	46.7	106.3
9.	Besleti	81.5	340	3.53	43.3	0.111	12.0	6.85	84.0	2.5	4.35
10.	Celasuri	220	1280	13.2	60.0	0.416	84.2	48.5	220	27.4	21.1
11.	Majarka	114	408	5.1	44.7	0.161	15.9	9.05	79.3	5.0	4.05
12.	Kodori	2030	1680	132	65.0	4.17	1295	754.0	371	362	392
13.	Tumush	62.2	174	1.64	26.3	0.052	3.35	1.9	30.5	0.85	1.05
14.	Dgamish	120	350	4.32	36.0	0.136	9.0	5.1	42.5	1.85	3.25
15.	Tshenistskali	61	171	1.62	26.4	0.051	3.35	1.9	31.1	0.8	1.1
16.	Mokva	336	700	18.1	53.9	0.571	46.8	27.55	81.9	8.3	19.25
17.	Galidzga	483	880	29.4	60.9	0.928	94.7	54.6	113	21.6	33.0
18.	Okumi	265	520	14.5	54.7	0.458	34.5	19.75	74.5	7.2	12.55
19.	Channel Eristskali			100		3.15					
20.	Inguri	4060	1840	39.5		1.247	450	260		78	182
				165*	40.6*	5.207*	2700*	1500*	385*	490*	1010*
21.	Khobi	1340	560	50.5	37.7	1.594	206.8	121.2	90.4	39.5	81.7
22.	Rioni, north delta	13400	1084	300	31.6	9.47	3500	2050	280	620	1430
23.	Rioni, south channel			124		3.91	2910	1705		510	1195
24.	Supsa	1130	970	50.1	44.3	1.581	246	143	126	46.0	97.0
25.	Natanebi	657	830	24.5	37.3	0.773	146.5	84.9	129	36.2	48.7
26.	Kintrishi	291	835	16.7	57.4	0.527	22.3	12.6	43.2	6.9	5.7
27.	Chakvistskali	172.6	740	12.5	72.4	0.394	19.0	10.6	61.4	8.5	2.1
28.	Korolistskali	55	500	3.8	69.1	0.200	8.30	4.6	83.6	3.5	1.1
29.	Chorokhi	22100	1530	267	12.1	8.43	8440	4920	222	2310	2610

* Before flow regulatio

It should be noted that research of sediments discharging from rivers into the sea should be considered as a result of the process of erosion. It should also be noted that data on river sediments from different sources most often include only the suspended load. Observations on bed load have been conducted only in very few cases.

Sea factors influence the river-mouth offshore sedimentation. Here, two zones of sedimentation can be distinguished: (i) a zone of wave action and (ii) a zone located below the wave base level (Neveski, 1967). A large amount of sediment is transported in form of bed load and coarse suspended load, forming submarine detritus fans and the submarine part of the delta. Usually, fresh river water transporting a large quantity of sediment does not mix with marine waters but spread into the 2-3 m thick surface layer, because the fresh river water is lighter than the marine water even if it contains sediments. For example, during the maximum degree of turbidity in the Inguri and Rioni rivers, the density of water is 1,006 kg/m^3, whereas the density of marine water is 1,017 kg/m^3 (Kutavaya, 1984).

In the marine area, after tearing off a river stream, the bottom bed loads move partially by force of inertia but, in general, under the wave influence. The suspended load falls out of the river stream as "sandy rain". Coarseness and intensity of this "rain" is very close to the river-mouth where it settles. Well offshore, the river flow discharges into the sea only non-beach forming clay fractions. Thus, river sediments accumulate in a coastal zone as continental or coastal sediments, but fine-grained sediment load moves over large areas and takes part in the process of marine sedimentation.

The most reliable data on river sediment discharge into the Black Sea belongs to the Caucasus rivers. Special studies have been carried out for this region besides regular hydrometric observations. (Joashvili, 1986; Khalatian, 1977; Khamaladze, 1978; Kochetov, 1991). In the Northeastern part of Russia, 920,000 m^3 of river sediment discharge into the sea, of which 320,000 m^3 are of coastal origin (beach forming) and 600,000 m^3 - marine sediments. In this region quantity of sediments discharging into the sea from rivers increases from North to South. After the Tuapse river-mouth, a drift of pebble is created along-shore (Kiknadze, 1970; Zencovich, 1958). This drift is locally interrupted by hydrotechnical constructions. The rivers Shapsukho (47,300 m^3), Tuapse (48,000 m^3), Psezuapse (33,800 m^3), Sochi (39,500 m^3) and Mzimta (98,000 m^3) discharge the largest number of sediments into the open sea. (Table 1).

In the Eastern part of the Black Sea (Georgian sector), the amount of river sediment increases sharply. The total volume of sediments represents 11,100 m^3, of which 4,400-m3 stay in the coastal zone and 6,700-m3 discharge into deeper parts of the sea. It is significant that, together with the volume, the coarseness of sediments also increases in this region. The Abkhazia and Adzhar rivers discharge the coarsest detritus in comparison with the other rivers discharging into this part of the sea. Of the total sediment volume, more than 90 % is discharged by large rivers, such as the Bzibi, Kodori, Inguri, Rioni and Chorokhi (Table 2). In the Georgian sector of the sea, submarine canyons play the main role by distributing 2.10^6 m^3 sediments to the deep sea. Large submarine canyons are found off the river-mouths of the rivers Chorokhi, Supsa, Inguri, Kodori and Bzibi. It should be noted that the sediment load of the Inguri is reduced by 83 % since 1977, due to the construction of a concrete dam. Because of the runoff regulation, the volume of sediments of the river Rioni is reduced by one third.

The rivers of Turkey discharge into the Black sea 9.7 10^6 m^3 of marine sediments. Of this total, 6.6 10^6 m^3 belong to large rivers, such as the Yeþilýrmak, Kýzýlýrmak, Filyos and Sakarya. A large quantity of sediments is discharged by small rivers in the eastern part of Turkey (1.9 10^6 m^3). The minimum average of specific sediment discharge (m^3/km^2 - yr.) has been observed in the European part of Turkey (Table 3). Due to the runoff regulation, the total volume of sediments delivered by the rivers Yeþilýrmak, Kýzýlýrmak and - to a less extent - by the Sakarya, has been drastically reduced.

Some Bulgarian rivers (Fakiiska, Sredetska, Aitoska, Provadiiska) discharge into the coastal lakes before reaching the sea. Due to this, their sediments are trapped in the lakes. The total volume of sediments discharging into the Western part of the sea does not exceed 460,000 m^3 annually (Table 4) Dimitrovetal.,1997).

In the Romanian sector, the Danube discharges into the sea 31.680 10^6 m^3 of sediments. The specific sediment discharge of this river is 38,8 m^3/km^2, (Bondar and Blenda, 1997).

TABLE 3. Rivers of the southern coast.

Rivers	Basin area, 1000 km^2	Average altitude, m	precipitations, mm	Water flow		Sediment load		
				l/sec km^2	km^3/yr.	1000 t/yr.	1000 m^3/yr.	m^3/km^2 yr.
From Corochi to Yesilýrmak (r.r. Abiviche, Firtina, Colopotamos Istila, Yalbulu, Degermen, Fol, Aksu etc.)	24	800	1400	15.0	11.36		(1900)	80
Yesilýrmak	36.1	650	500	4.30	4.89	360 19000*	210 11200*	 310*
From Yeþilýrmak to Kýzýlýrmak	2.5	300		12.0	0.94		(175)	(70)
Kýzýlýrmak	78.2	810	400	2.32	5.74	460 23000*	270 13500*	 170*
From Kýzýlýrmak to Filyos	9.9	350		10.0	3.12		600	(60)
Filyos	13.0	700		6.97	2.85	4200	2500	190
From Filyos to Sakarya	3.6	(300)		10.0	1.13		220	(60)
Sakarya	58.2	430	450	2.48	4.54	6200 8800*	3600 5200*	 90.0*
From Sakarya to Rezovska	4.8	(200)	700	9.60	1.45		250	(50)

- Before flow regulation

TABLE 4. Rivers of the Western coast.

N	Rivers	Basin area, km^2	Basin average altitude, m	Water flow			Sediment load		
				m^3/sec	l/sec. km^2	km^3/yr.	1000 t/yr.	1000 m^3/yr.	m^3/km^2 yr.
1.	Rezovska	183.4		0.79	4.30	0.025	17.4	10.2	55
2.	Veleka	995	362	8.76	8.80	0.276	77.9	45.8	46
3.	Karaagatch	224.3		0.96	4.28	0.030	21.3	12.5	55
4.	Dyavolska	133.2		0.57	4.28	0.018	12.7	7.47	56
5.	Ropotamo	248.7	201	1.17	4.70	0.037	23.6	13.9	56
6.	Aheloy	141.0		0.61	4.33	0.019	13.4	7.88	55
7.	Hadjiska	355.8	230	1.53	4.30	0.048	33.8	19.8	55
8.	Dvojnitza	478.8		2.06	4.30	0.065	45.5	26.7	56
9.	Panairdere	58.2		0.25	4.29	0.008	5.5	3.23	55
10.	Shkorpilovska	78.7		0.34	4.31	0.011	7.5	4.41	56
11.	Kamchia	5358	327	19.25	3.59	0.607	462.0	271.7	50
12.	Kranevska	84.5		0.36	4.26	0.011	8.0	4.70	55
13.	Batova	338.8	252	0.73	2.15	0.023	35.4	20.8	61

TABLE 5. Rivers of North - Western coast

Rivers	Basin area, 1000 km^2	Water flow			Sediment load		
		m^3/sec	km^3/yr.	l/sec. km^2	1000 t^3/yr	1000 m^3/yr.	m^3/km^2 yr.
Danube	817	6268	198	7.67	53867	31680	38.8
Dniester	72.1	367	11.6	5.1	1730 2500*	1000 1500*	 20.8*
Ingul	9.7	18.5	0.60	1.9	126	75	7.8
South Bug	63.7	139	4.4	2.2	1200	700	11.0
Dnieper	503	1560	49.2	3.1	1060 2100*	630 1250*	 2.5*

- Before flow regulation

TABLE 6. Rivers of the Crimea

N	Rivers	Basin area, km^2	Basin average altitude, m	Water flow			Sediment load		
				m^3/sec	l/sec. km^2	km^3/yr.	1000 t/yr.	1000 m^3/yr.	m^3/km^2 yr.
1.	Alma	633	500	1.40	2.2	0.044	44.3	24.6	38.8
2.	Kacha	110	800	1.32	12.0	0.042	12.1	6.72	61.1
3.	Kokozka	836	910	1.17	1.4	0.037	25.9	14.4	17.2
4.	Belbek	270	730	2.16	8.0	0.068	32.4	18.0	66.6
5.	Chornaia	47.6	730	1.47	31	0.046	0.57	0.32	6.72
6.	Derekoika	49.7	730	0.48	9.8	0.015	2.78	1.54	30.9
7.	Ulu - Azen	64.8	610	0.56	8.7	0.017	6.48	3.6	55.5
8.	Demerji	53	460	0.13	2.4	0.004	4.66	2.58	48.6
9.	Taraktash	153	340	0.06	0.4	0.001	2.65	1.47	9.60

The large rivers of Ukraine are regulated and the volume of alluvium volume is drastically reduced. All these rivers discharge into brackish lagoons where they deposit about 2.4 10^6 m^3 of sediments. For this reason, they pour only a small amount of sediment into the sea (Table 5). Regarding the Crimean rivers, the sediment load is estimated at 75,000 m^3 only (Table 6) (Dedkov and Mozjerin, 1984).

The seasonal supply of river sediments to the sea is variable. All large rivers are characterized by powerful high spring water when a large amount of sediments discharges into the sea. There are autumn-winter floods in small rivers, but the total volume of sediment transported by them is not important, playing only an insignificant role in the process of marine sedimentation. It should be noted that the volume of runoff and sediment in these rivers varies from year to year.

The coefficient of variation regarding the runoff of large rivers does not exceed 0.2, but for suspended load, the values range between 0.6 - 0.9. The size of grain alluvium is also variable, which in turn influences the coastal dynamics and the granulometric composition of marine sediments on a small scale.

Besides the river sediments, about 17 10^6 m^3 of sediment is provided to the Black Sea by coastal abrasion Shuiski, 1981). According to Aibulatov and Novikova (1984), in the Black Sea a longs-shore drift of deposits is bound up within the river runoff. The capacity and direction of the drift is controlled by the topography of the coast, the bathymetry of the shelf as well as the nature of the predominant stream.

CONCLUSION

The total fresh water discharge into the Black Sea is 353.3 km^3 per year. The rivers pour into the Black Sea about 51.6 10^6 m^3 of sediments taking part in the present process of sedimentation.

This study is the first attempt to provide a quantitative estimation of the river sediment load in the Black Sea. This estimation will be more refined as more data become available. Therefore, it is possible to determine more accurately the sediment drift, processes of sedimentation, pollution and many other problems which exist today in the whole Black Sea.

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SEDIMENT AND FRESHWATER DISCHARGES OF THE ANATOLIAN RIVERS INTO THE BLACK SEA

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ABSTRACT

The Anatolian Rivers supply annually 24 million tons of sediments and 40 km^3 of fresh water into the Black Sea. At present, compared to the other rivers discharging into the Black Sea, the Anatolian river sediment input constitutes 20% of the total river sediment load. Prior to the construction of two dams near the mouth of the Yeþilýrmak and Kýzýlýrmak, respectively in 1981 and 1988, this load was 53 million ton/y. The sediment load transported by the Kýzýlýrmak and Yeþilýrmak represents 17 million and 13 million ton/y respectively, prior to the completion of dam constructions. The high relief and steep slopes of the Pontide Mountains extending parallelly to the coast are the major cause of this high sediment load. The sediment load and fresh water input of the Anatolian rivers vary according to the contrast of relief and the amount of precipitation, both decreasing from east to west in the Black Sea Region.

INTRODUCTION

The Black Sea is the world's largest anoxic basin isolated from the ocean and situated between the folded alpine belts of the Pontic Mountains southward (Turkey) and the Caucasus and Crimea ranges northward (Ross, 1974) (Figure 1). The straits of Bosphorus and Dardanelles and the Sea of Marmara connect the Black Sea with the Mediterranean Sea. The Black Sea covers an area of 432,000 km^2 and represents a volume of 534 km^3 (Ross, 1974; 1977). The shelf area off the Danube is very extended (more than 190 km) due to the accumulation of a considerable amount of sediments carried by the Danube, Dnestr, Bug, and Dnepr rivers. Along the Anatolian coast, the shelf is about 20 km long. The basin slope is steep and dissected by submarine canyons off the Anatolian coast, whilst it becomes smoother off the Rumanian/Bulgarian shelf (Ross, 1974; Erinç, 1958). The western and northern coastal regions of the Black Sea are very low, whereas the southern (Pontide Mts; max. 3,937 m) and eastern (Caucasus Mts; max. 4,040 m) coastal regions display higher elevations.

The Black Sea receives river inputs from half Europe and part of Asia. The land-derived terrigenous material constitutes an important component of the recent sediments of the Black Sea basin. The sediment input from rivers is mostly trapped in the Danube Fan and Sea of Azov in the northern and northwestern parts of the Black Sea, whereas the river input from the southern Black Sea is rapidly transported into the deep basin due to the narrow shelf (Ross and Degens, 1974; Shimkus and Trimonis, 1974). The recent sediments (Unit 1) of the Black Sea , which have been depositing along the last 3000 years consist of an alternating sequence of biogenic carbonate-rich light (mostly coccolithophorid *Emiliana huxleyi*) and terrigenous dark microlayers (Müller and Stoffers, 1974; Ross and Degens, 1974). The seasonal changes in sedimentation are preserved in form of these laminated sequences. The deposit of the black laminae of this unit is related to an important lithogenic flux caused by high river inputs during February-May (Honjo *et al.*, 1987; Hay *et al.*, 1990, 1991; Duman, 1994).

The Anatolian coastline of the Black Sea is 1,625 km long (Darkot, 1975), extending from the border westward to the Georgian border eastward. Along this coast, five major rivers and various small rivers discharge their water and solid particles into the Black Sea. The previous studies concerning river inputs into the Black Sea include those carried out by Shimkus and Trimonis (1974), Tolmazin (1985), Milliman and Syvitski (1992) and Hay, (1994). In this study, we present a comprehensive analysis of 20-year data on the fresh water and suspended sediment fluxes of five major and some small Anatolian rivers into the Black Sea. This study aims at determining the spatial and temporal variations of the sediment and fresh water fluxes from the Anatolian rivers into the Black Sea, and discuss the effects of natural and man-made factors, such as relief contrast, precipitation and dam construction on the sediment flux. Fresh water and suspended sediment discharges of the Anatolian rivers into the Black Sea were computed on the basis of data from the Directorate of Electrical Research Works (EIE) DATABASE (EIE, 1993). The sampling stations used in this study are located close to the river mouths (Figure 2). On the basis of about 20-year data, the following analyses were carried out:

(i) Total fresh water and suspended sediment inputs of the Anatolian rivers;
(ii) Comparison of the Anatolian river inputs with those from other rivers discharging into the Black Sea;
(iii) Annual variations in the average fresh water and suspended solid discharges of each river, and
seasonal variations in the fresh water and suspended solid discharges of the Anatolian rivers.

TOTAL FRESH WATER INPUT AND SUSPENDED SEDIMENT DISCHARGES

There are five major rivers, namely Sakarya, Filyos, Kýzýlýrmak, Yeþilýrmak, and Çoruh, and several small rivers, such as Karasu, Devrekani, Harþit, Ýyidere, and Melet flowing into the Black Sea from Anatolia (Figure 2, Table 1). Compared to the other rivers discharging into the Black Sea, the majority of the Anatolian rivers is generally shorter, with smaller drainage areas and linear drainage patterns. The Sakarya, Kýzýlýrmak and Yeþilýrmak, however display various drainage patterns, with its tributaries, forming a fluvial network. At present, the Anatolian rivers carry annually 40 km^3 of fresh water and 24 million ton of sediments into the Black Sea.. The Çoruh river has the highest water discharge (6.3 km^3/y) with a 16%, followed by the Kýzýlýrmak (15%), Sakarya (14%), Yeþilýrmak (13%), and Filyos (7%) (Figure 3).

The major rivers from the central and eastern regions carry the main part of the sediment load into the Black Sea. The Çoruh River delivers the highest sediment load with 7.5 million ton/y, constituting the 31% of the total load from Anatolia. The small rivers of the Eastern region (17%), Sakarya (16%), Filyos (16%), and the small rivers of the Central region (11%) provide the other parts of the major contribution. Kýzýlýrmak and Yeþilýrmak rivers appear to contribute only 2% and 1%, of the sediment load, respectively (Figure 3). However, prior to the completion of dam constructions in 1988 and 1981, the Kýzýlýrmak and Yeþilýrmak rivers provided the Black Sea with the largest amount of sediments from Anatolia, with a flux reaching respectively 31% and 24% of the total at that time.

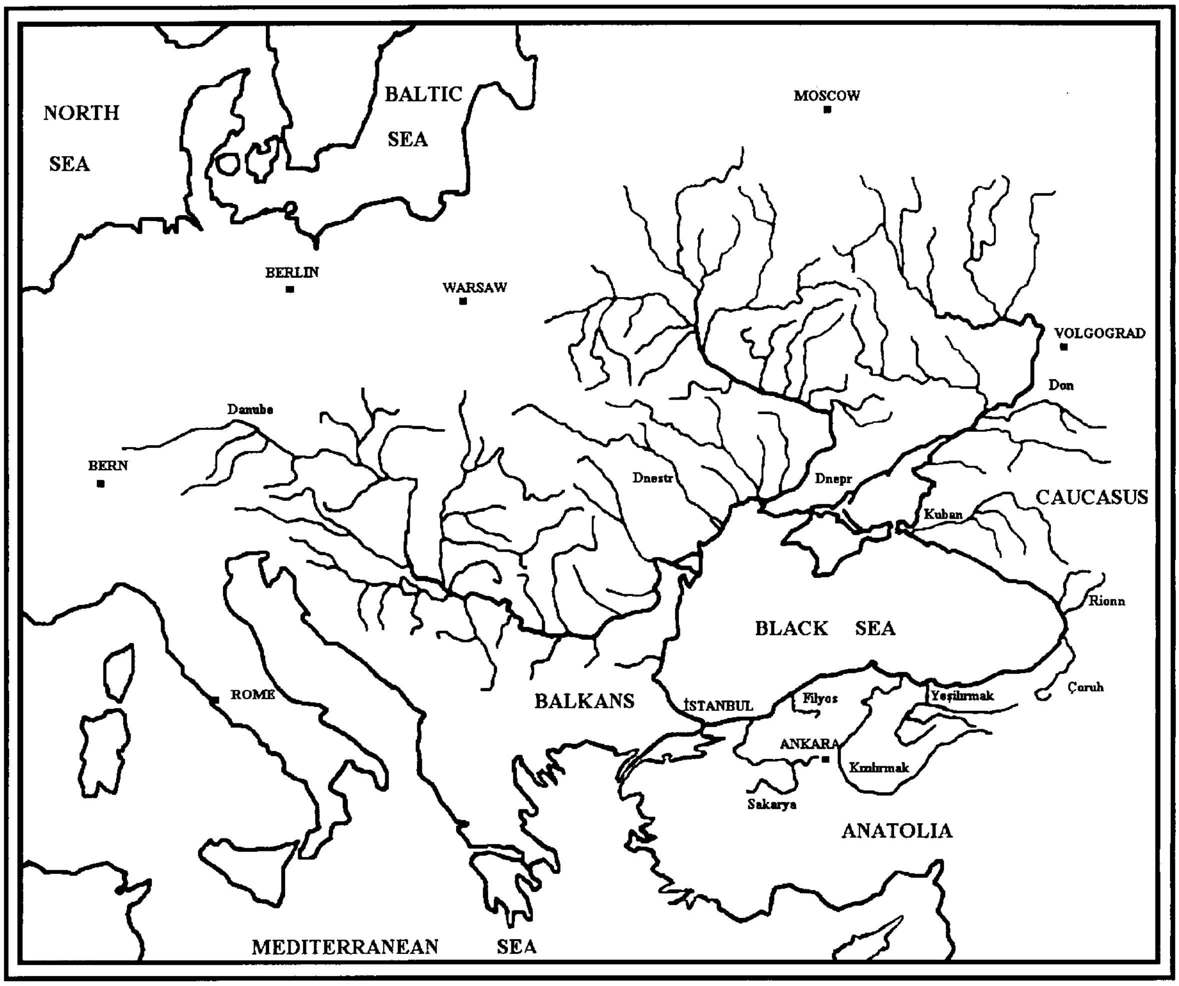


FIGURE 1. Drainage areas of the Black Sea (from Müller and Stoffers, 1974).

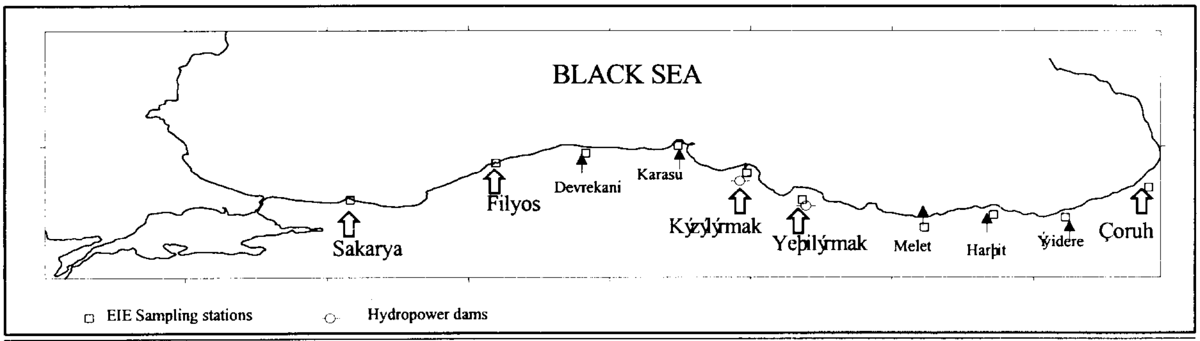


FIGURE 2. Map showing sampling stations on Anatolian rivers discharging into the Black Sea.

TABLE 1. Anatolian rivers discharging in the Black Sea: their length, drainage area, fresh water and sediment discharges

Rivers	Length (km)[1]	Drainage A. (km^2)[2]	Water (km^3/yr)[3]	Sediment (10^6 ton/y)[3]	Sediment (Pre-dam) (10^6 ton/y)[3]
Sakarya	824	56,504	5.6	3.8 (1972-90)	4.6
Filyos	228	13,156	2.9	3.7	3.7
Small Western R.[4]		7,700	2.4	1.4	1.4
Small Central R. [4]		14,600	4.5	2.7	2.7
Kýzýlýrmak	1355	78,646	5.9	0.44[5]	16.7
Yeþilýrmak	519	36,129	5.3	0.33 (1979-84)	12.5
Small Eastern R.[4]		22,200	6.8	4.0	4.0
Çoruh	466	19,984	6.3	7.5	7.5
Total		248,919	39.7	23.9	53.7

[1] Statistical yearbook of Turkey, 1985; [2] Atalay, 1994; Ýzbýrak, 1972; EIE, 1993; [3] This study; [4] Hay, 1994; [5] calculated assuming the same sediment load reduction rate of the Yeþilýrmak.

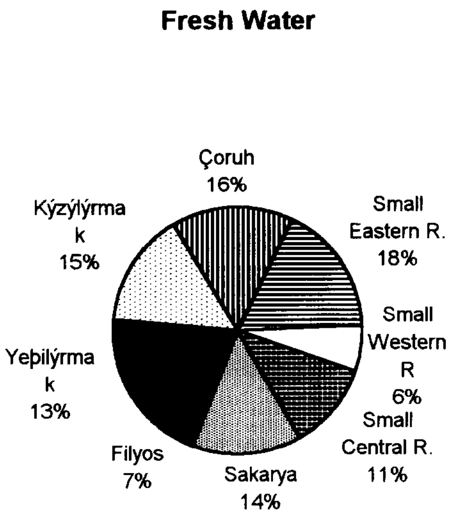
RIVER INPUTS FROM THE ANATOLIAN RIVERS COMPARED TO OTHER RIVERS DISCHARGING INTO THE BLACK SEA

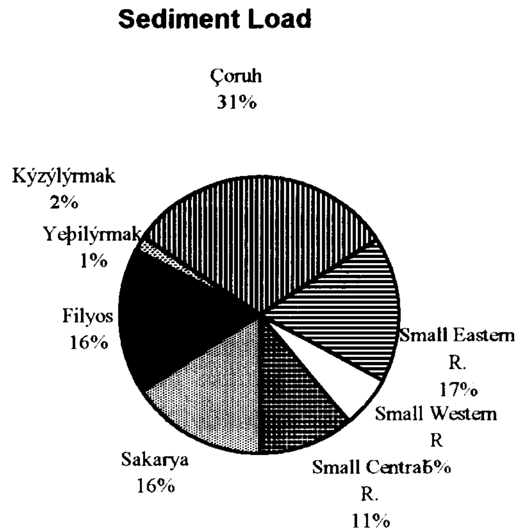
The main fresh water source for the Black Sea is the Danube, with a 60% of the total water input. The Dniepr is in the second, whereas Don and Anatolian Rivers are in the third order (Table 2, Figure 4). Danube carries riverine suspended particles with a 60% of the total load. Anatolian Rivers contribute 20% of the total load, being in the second order of suspended sediment supply. Prior to the dam constructions, however, Anatolian Rivers provided the 30% of the total load.

A substantial amount of the sediments carried by the northern rivers flowing over the wide European plain areas into the Black Sea are retained by the Danube fan and the Sea of Azov. On the other hand, the river input from the Anatolian rivers pours into the narrow continental shelf; it is rapidly transported to the deep basin of the Black Sea via the submarine canyons or as suspension load.

AVERAGE ANNUAL FRESH WATER AND SEDIMENT INPUTS OF THE ANATOLIAN RIVERS

The annual average water and suspended sediment discharges of the rivers show similar fluctuations over the last 20-year period (Figure 5). Both fresh water and suspended sediment discharges of the Çoruh River are almost similar throughout the years. Suspended sediment discharge of the Yeşilırmak River, however, shows an abrupt decrease in 1979, because of the effect of a dam construction (Suat Uğurlu Dam) between 1975 and 1981. The annual average of suspended sediment load of the Kızılırmak River displays a fall in 1974 and 1986 without significant corresponding decreases in the fresh water discharges. The construction of the Altınkaya Dam on the Kızılırmak River was started in 1980 and completed in 1988. The effect of this dam on the sediment yield downstream could not be directly evaluated since the sampling at this station was ceased after 1987. A similar sediment trapping efficiency can be considered for the Altınkaya Dam on the Kızılırmak River as for the Suat Uğurlu Dam on the Yeşilırmak River, because both dams are located at similar geomorphologic setting and similar distances from the respective rivers. The annual average of suspended load of the Sakarya River seems to have decreased since 1972 with the completion of the Gökçekaya dam, located close to the upper course of the Sakarya river. The annual sediment load of Filyos was significantly variable, but the fresh water input was uniform during between 1970 and 1990.





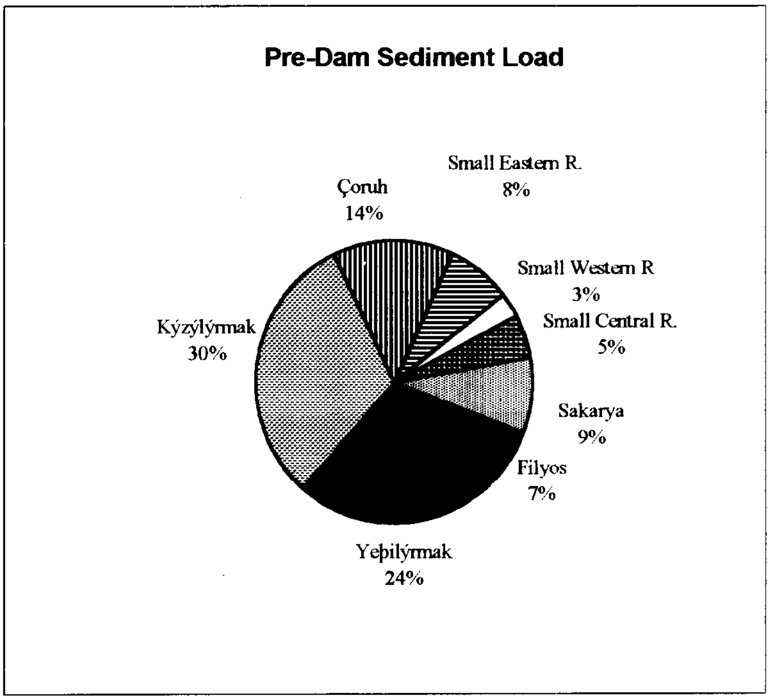
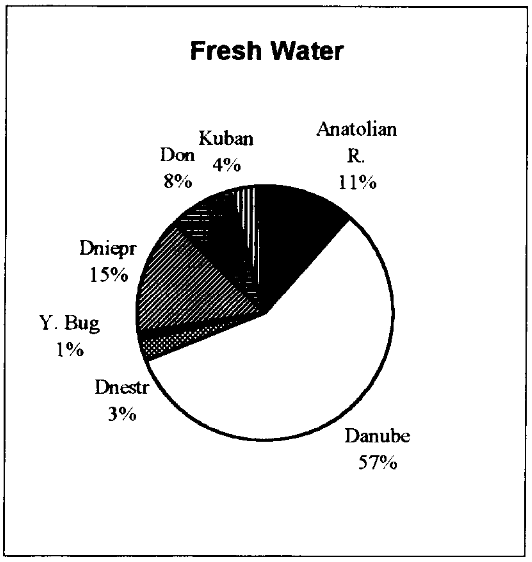


FIGURE 3. Comparison of total fresh water and suspended sediment loads of the Anatolian rivers (< 1% contributions are not shown on pie diagrams).



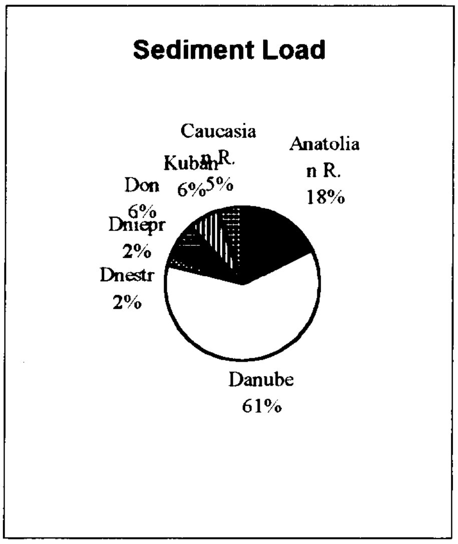


FIGURE 4. Comparison of total fresh water and sediment loads of rivers discharging into the Black Sea (less than 1% contributions are not shown on pie diagram).

TABLE 2. Drainage area, Fresh water and sediment fluxes of rivers discharging into the Black Sea (from Shimkus and Trimonis, 1974; Müller and Stoffers, 1974; Tolmazin, 1985; Ross, 1977; + This study).

River	Drainage Area (km^2)	Water (km^3/yr)	Sediment ($10^6 t/yr$)
Danube	816,000	201	83.0
Dniester	75,200	10.0	2.50
Y. Bug	34,000	3.0	0.53
Dneiper	574,610	52.0	2.12
Don	422,000	28.0	7.75
Kuban	63,500	12.8	8.40
Rioni	13.4	13.5	8.50
Caucasian Rivers			6.79
Bulgarian coast		3.0	0.50
+Anatolian Rivers	248,919	39.7	23.9

SEASONAL VARIATIONS OF FRESH WATER AND SEDIMENT INPUTS OF THE ANATOLIAN RIVERS

The fresh water discharge of the Çoruh river starts to increase rapidly in March and it decreases in July (Figure 6). As in the case of the Yeþilýrmak and Kýzýlýrmak, the maximum fresh water input is between March and May. The input displays an increasing trend also in January and a fall during the summer. In the small rivers of the eastern region, such as the Harþit, Ýyidere and, the highest discharge of fresh water occurs between March and July, and the lowest in late summer. Fresh water inputs of the Sakarya and Filyos rivers increase in December, and decrease in April, reaching the lowest values during summer.

The Çoruh River displays high sediment loads between March and June (Figure 7). High-suspended sediment loads occur in rivers Kýzýlýrmak and Yeþilýrmak from February to June. Suspended sediment loads carried by the small rivers of the eastern region show an increase in March and decrease in August. The maximum discharges of suspended sediment loads of the Sakarya and Filyos rivers occur in different months; an irregular pattern has been observed during the last 20 years. However, the average suspended load distributions of these two rivers begin to increase in December and decrease in June.

All the rivers in the eastern and central regions of the Anatolian Black Sea coast have similar characteristics, whereas the western rivers (Sakarya and Filyos) seem to be influenced by climatic and topographical conditions different from those in the drainage areas of the other rivers.

FACTORS CONTROLLING THE SEDIMENT LOAD OF THE ANATOLIAN RIVERS

The suspended sediment loads of rivers are controlled by a number of natural factors, such as: relief of the drainage basin, drainage basin area, amount of water discharge, geology of the river basin, climate, presence of lakes along the river, and human activities (i.e., deforestation, agriculture and building of dams) (Miliman, 1980; Berner and Berner, 1987).

The suspended sediment load of most rivers is influenced by more than one of these factors in combination. The relief of the Anatolian coasts seems to have the major effect on the high sediment input of the rivers.

Despite the small drainage areas, the Anatolian rivers deliver a high sediment flux to the Black Sea, because of the high relief of the Pontides and the absence of flood plains. The effect of the relief on the sediment load is observed among the Anatolian rivers. The greater sediment input comes from the rivers in the eastern region compared to those in the western region, with an increasing load as follows: > Kýzýlýrmak>Yeþilýrmak>Çoruh>Sakarya.

The amount of fresh water discharged by rivers has a great effect on the suspended sediment load in the Anatolian rivers. Seasonal variations of the fresh water and sediment load of the rivers Çoruh, Yeþilýrmak, Kýzýlýrmak, and small rivers of the eastern region (Harþit, Ýyidere and Melet) display quite similar trends (Figures 5 and 6). The snow melt in the mountain peaks of the eastern region contributes fresh water to small rivers. On the other hand, in the western part, the relation between the amounts of fresh water and sediment load in the Sakarya and Filyos rivers is not so strong as for the eastern rivers.

Along the Anatolian coasts, the annual precipitation is 600 mm in the western region, and more than 2000 mm in the eastern region, with an annual precipitation increasing with topography from west to east (DMI, 1974). The precipitation trends in the drainage areas of the Çoruh, Harþit, Ýyidere, Yeþilýrmak, and Kýzýlýrmak rivers differ from those of fresh water and sediment load. The eastern rivers receive the highest precipitation (rainfall and snowfall) between late autumn and late winter. An important part of these precipitations are preserved in the mountains as snow and glaciers. During the spring, the melting of this snow contributes a considerable amount of water to these rivers. Decreasing precipitation westwards has a more important effect on the sediment load of rivers, becoming an important factor in the sediment load of rivers of the western region (i.e., Filyos and Sakarya rivers) (Figure 8). In this region, the seasonal variation of sediment load follows the precipitation trend.

The drainage basins of the rivers is underlain by a variety of volcanic rocks and flysch, including basalt, andesite, dacite (Upper Cretaceous to Eocene) tuffs, agglomerates sandstone and shale (Brinkmann, 1974, 1976). High susceptibility to erosion of some rock units, such as tuffs and flysch, is also an important factor contributing to a large amount of sediment load in the Anatolian rivers.

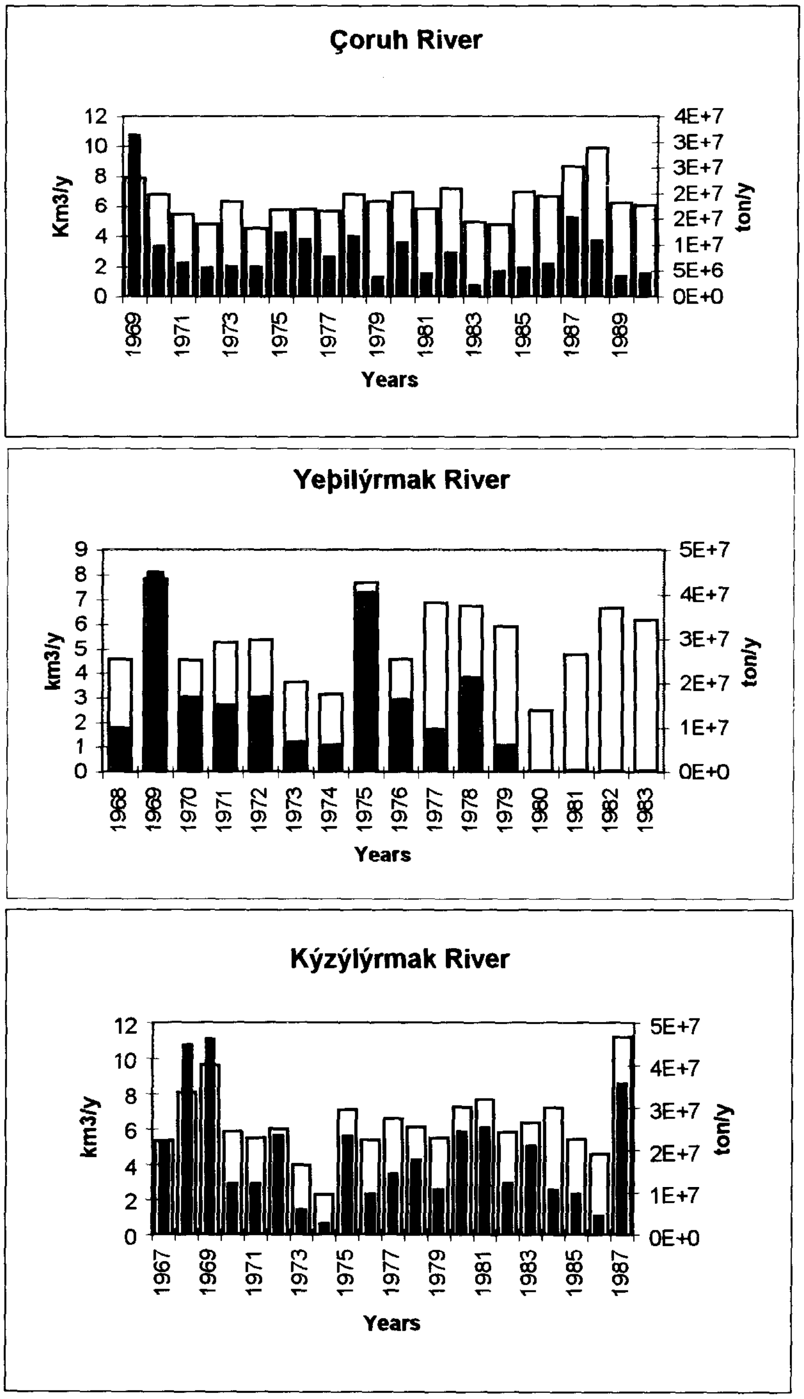


FIGURE 5 . Variations of annual fresh water and sediment inputs by Anatolian rivers.

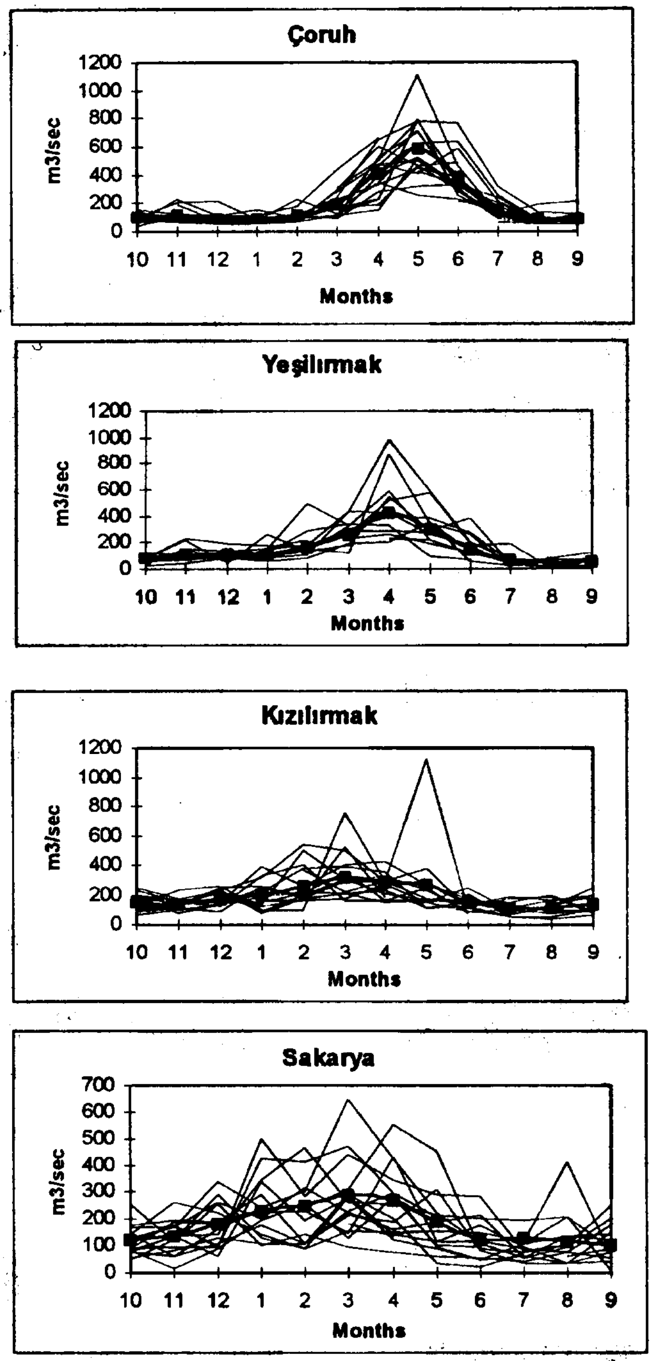


FIGURE 6. Seasonal variations of fresh water in Anatolian rivers (based on 20-year data) (lines with black square denote 20-year averaged).

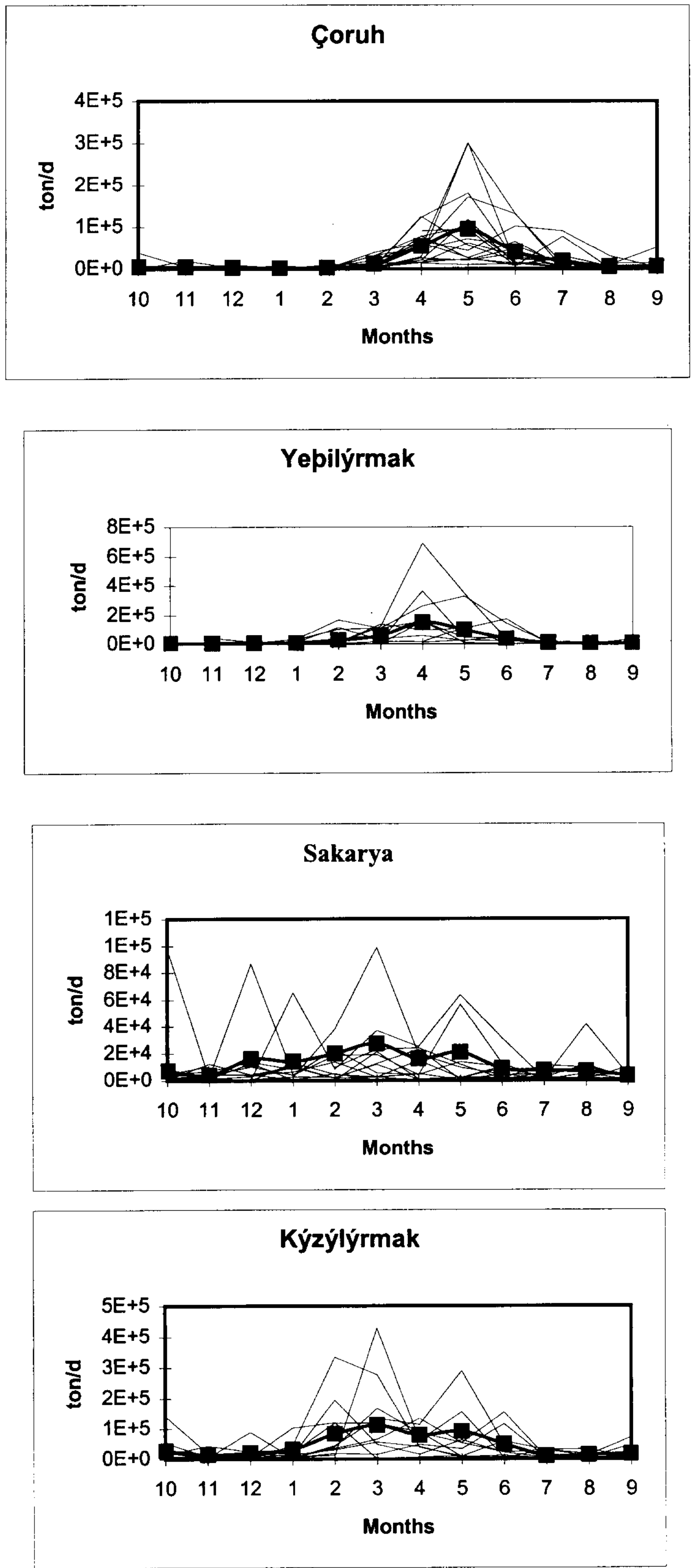


FIGURE 7 Seasonal variations of suspended sediment load in Anatolian rivers (based on 20-year data) (lines with black square denote 20-year averaged

There is no lake in the drainage areas of the anatolian rivers. The dam constructions built near the mouths of the rivers kýzýlýrmak and yeþilýrmak, however, have drastically reduced the amount of sediment discharges of these rivers since 1988 and 1981, respectively. The analysis of data collected over 20 years indicates that several dams in the upper drainage areas of the major rivers since 1970 have no significant effect on the amount of sediment flux (figure 7).

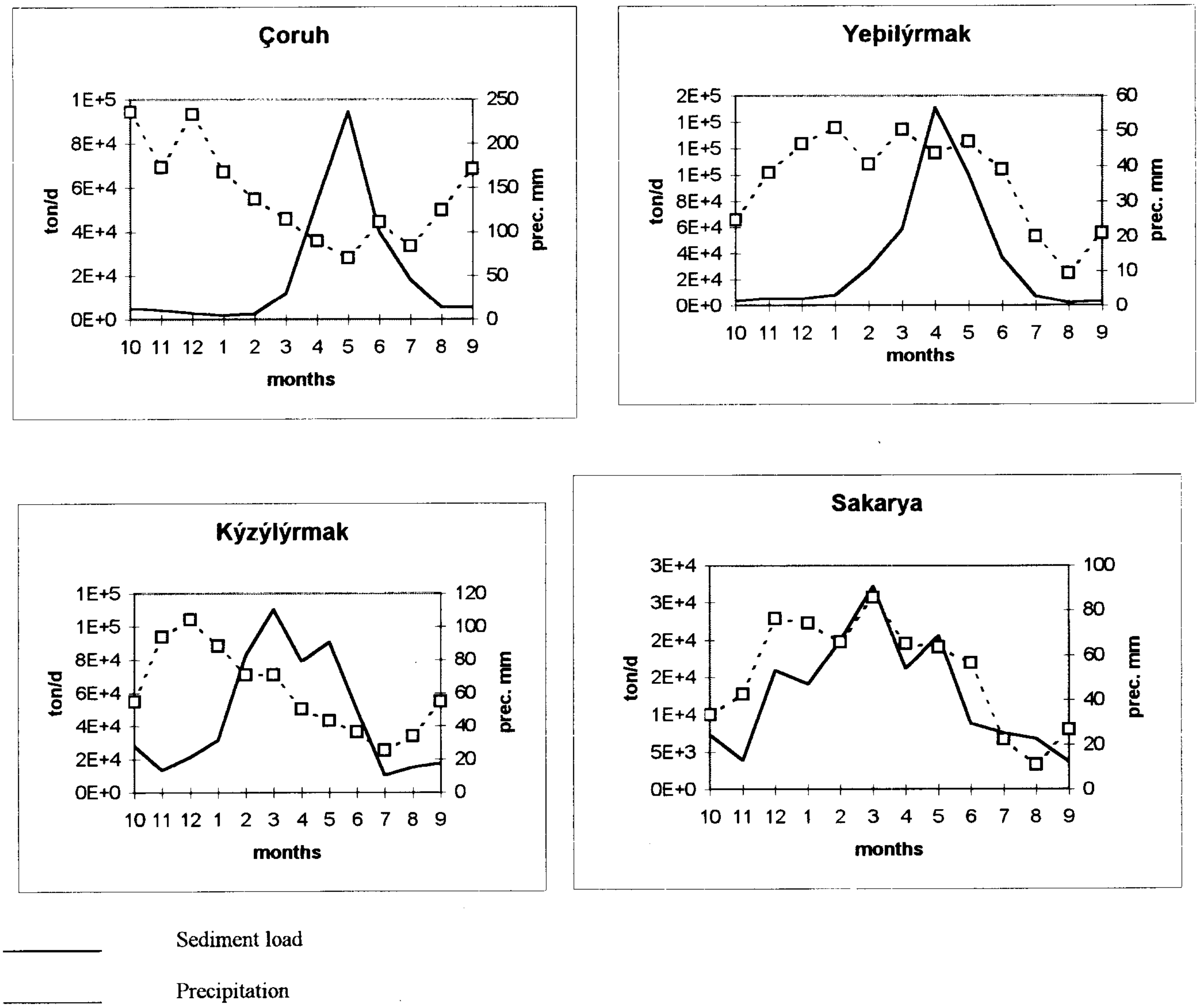


FIGURE 8. Sasonal variations of precipitation and sediment load in the Anatolian rivers discharging into the Black Sea (based on 20-year data).

CONCLUSION

The Anatolian rivers presently contribute 24-million ton/y sediment river load and 40-km3/y fresh water into the Black Sea. The total suspended sediments delivered by the Anatolian rivers constitutes 20% of the total river load. Before the recent dam constructions on the rivers Yeþilýrmak and Kýzýlýrmak, the total river sediment flux to the Black Sea by the Anatolian rivers was 53 million ton/y, representing 30% of the total load. Such a high amount of sediment input is principally supplied from the high mountainous terrain extending parallel to the coast. The differences between sediment

sediment fluxes of the eastern and western Black Sea rivers is due to the difference in the topographical relief of the two regions. The topographic differences between these regions also determine the amount of precipitation in the lower drainage areas and water discharge of the rivers. As a result, water discharges of the rivers in the eastern region are higher than in the western region. The seasonal variation in the fresh water discharges of the rivers is generally in correlation with the variation in the sediment load; and the variation in precipitation indirectly controls the seasonal variations in the sediment load. This is particularly apparent in the case of the rivers in the central and eastern regions. In the western region, fresh water and precipitation factors together influence the amount of sediment load. The sediment input by the Anatolian rivers delivers the terrigenous sediment onto the narrow shelf, then this sediment is transported to the deep basin via the submarine canyons.

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THE SOURCE PROVINCES IN THE WESTERN BLACK SEA

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ABSTRACT

Four basic geological structures have been identified in the western part of the Black Sea. They are distinguished by their heterogeneous lithological structure and mineralogical composition. The total watershed area covers 16,000 km^2. The annual average of the river water flow amounts to 1.2 km^3 and the quantity of terrigenous material imported represents 780,600 t/year.

Of the total 371-km length of the Bulgarian coastline, there are 237 km strongly affected by erosion. From this coastline, about 575.3t of material is transported annually into the sea. The total amount of sediment originating from coastal erosion and river transport is up to 1,356,000 t/year.

The mobilization of the sediment material from the adjacent land takes place under moderately humid climate conditions. Typical thin weathering crusts are being formed here, and mechanical disintegration is predominant for the sediment material.

Three source provinces have been identified according to the composition of terrigenous material in the coastal zone and on the shelf: the southern, central and northern provinces. They reflect the mineralogical composition of the adjacent land. The main source of terrigenous material in the western and northwestern parts of the Black Sea is the sedimentary load delivered by the Danube.

INTRODUCTION

The large diversity of geological formations constituting the Bulgarian coast of the Black Sea explains the assorted composition of beach and shelf deposits. The main structural elements (e.g., deep faults) intersect the shelf and the coast and divide the region into four main geological provinces: Eastern Moesian Platform, Lower Kamchiya Depression, Stara Planina and Sredna Gora zones (Figure 1).

The differences in the lithological structure and mineralogical composition of the geological formations constituting the main structural zones, allow to distinguish three main lithostructural regions as independent source provinces: the northern, central and southern provinces, respectively. The land boundaries between these provinces are drawn along an orohydrographical network of rivers running into the Black Sea. These provinces facilitate the transport of terrigenous deposits, eroded by exogenous processes, to the Black Sea basin. The total watershed area of the western Black Sea region is about 16,000 km^2 (Figure 1) and the average annual quantity of river water delivered to the Black Sea from this region is 1.2 km^3 (Table 1).

The total Bulgarian Black Sea coastline is 371 km long. Of this total, 237-km of coastline is affected by a strong erosion. The total quantity of sediment flux entering the Black Sea by coastal erosion and from the watershed area via the rivers amounts up to 1,356,000 t/yr (Table 1, 2).

SOURCE PROVINCES

The Southern Source Province

This province covers an area limited by Turkey towards the south, the Northern Transbalkan deep faults towards the north, and the Strandja mountain range towards the west. It is located within the Sredna Gora zone (Figure 1) which consists mainly of a Senonian volcano-sedimentary complex. This complex is composed of various lithologies, including andesite, trachyandesite, tuff, tuffite, agglomerate and various dyke rocks, and is covered with Neogene and Quaternary sediments. In its most southern part, the volcano-sedimentary complex has been built up by the alternation of conglomerate and breccia with a sandy matrix, arkosic sandstone and marl and limestone with tuffaceous intercalations. Pyroclastic rocks, characterizing most of the province, appear in the uppermost part of the section. Because of the high concentration of heavy mineral in the beach and submarine coastal slope sediments in the Burgas Bay, intensive studies are carried out in this province.

The Laramian intrusive masses are concentrated in a strip, occupying the coast and the adjacent land at the south of Burgas where Rosen's and Vurlybriag's intrusions are located. Rosen's intrusion follows the submarine coastal slope at a distance of 7 km from the coast. The intrusions have a complex structure and composition, and consist of monzosyenite, alkaline syenite, monzodiorite, leucosyenite, aplite and granite. Dykes commonly occur near the intrusive bodies and are composed of various kinds of rocks, including hornblendite, hornblende porphyry, gabbroporphyry and granite.

The Lower and Middle Sarmatian sediments of Crimean-Caucasian type are represented by clay, marl, sandstone and limestone relatively resistant to erosion, which compose the jutting capes between the towns of Nessebar and Pomorie. This is the reason why the Middle Sarmatian sediments are the intermediate collector of magnetite.

At the end of the Pliocene and the beginning of the Pleistocene, active tectonic movements, together with alterations in the climatic and paleogeographical conditions, caused considerable changes in the Balkan Peninsula. This stage is characterized by the deposition of boulder, rubble-granite and sandy-clay deposits, as observed at the east of the village Grudovo, near v. Novoseltzi. The boulder-rubble material consists of round quartz fragments with a sand-size quartz matrix. The quartz-rich nature and red color of the section support a granitic source for this sedimentary material and suggest a possibility of gold occurrence in the area. These sediments are generally accepted to be dated of the Pliocene, but the upper part of the section extends to the Lower Pleistocene (Villafranchian), due to the presence of some elephant (Archicodon meridionalis Nesti) remains (Popov, at all, 1964). In our opinion, the fluvial-bed load deposits have been formed during a low stand of the sea level and they have a duration equivalent to the Lower Pleistocene (Claudine) marine sediments on the shelf (Dimitrov, 1978).

The Holocene sediments in the lakes Vaja and Mandren have been observed in a belt of up to 50-m width. Beach and shallow-water deposits with two buried soil layers have been discovered in some of the drill-holes of "Transproject" in the Burgas Bay, attesting the frequent migration of the coastline and change of the sedimentation regime during the Holocene.

The mineralogical analyses of the beach sands and submarine coastal slope sediments show a high content of heavy minerals. The coarse aleurite (silt) sub-fraction of the sands at the Sunny Beach resort is enriched in magnetite (25.8%) and zircon (24.4%), whereas by the mouth of the Handjiiska River, the 0.1-0.05 mm fraction consists mainly of quartz and feldspar. In the region from St Vlas to Michurin the content of heavy fraction varies in a wide range from 5% to 95%; it contains magnetite, pyroxene, chromite, zircon, ilmenite, sphene, garnet, apatite, monazite and epidote (Tzvetanova-Goleva, 1974).

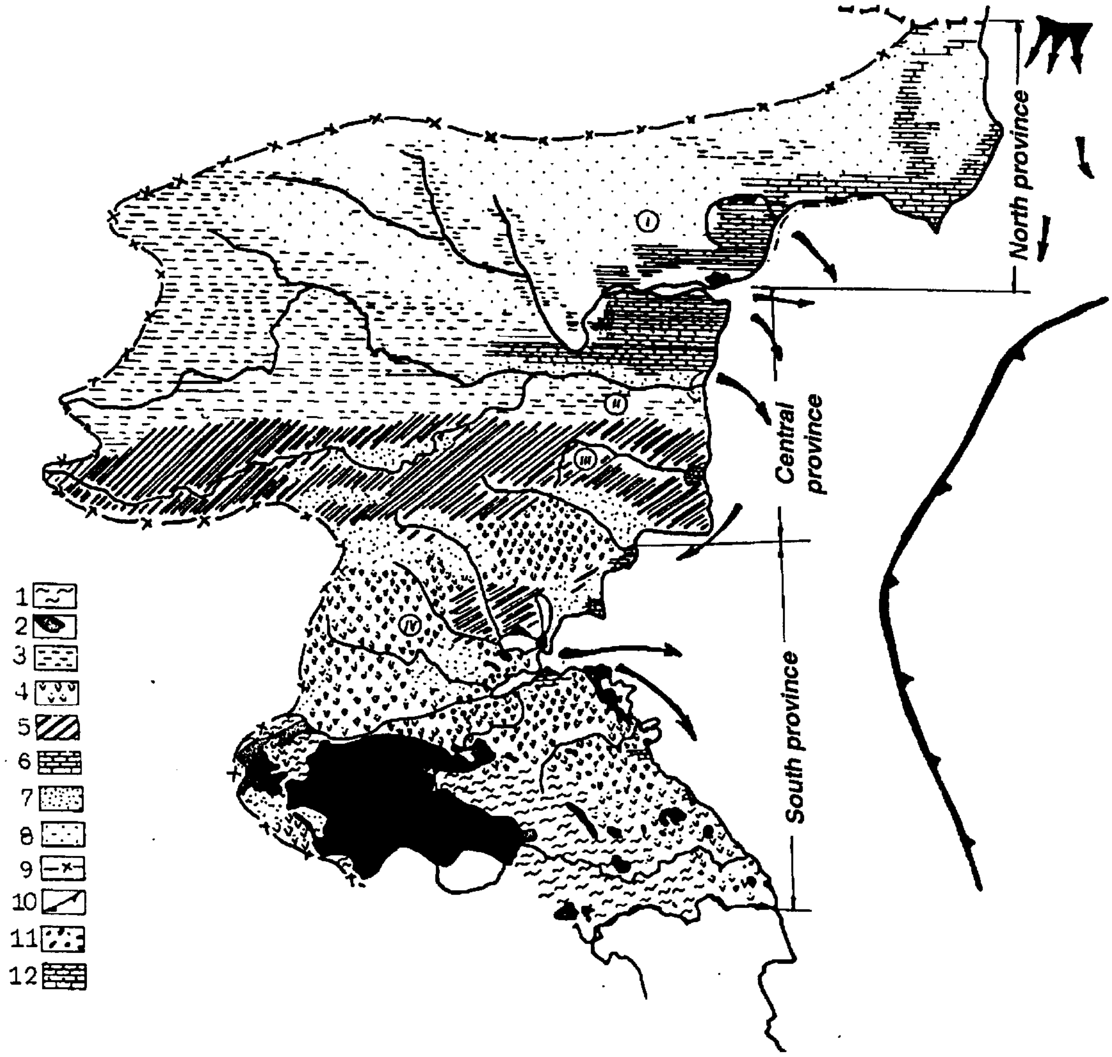

FIGURE 1. Lithologic-structural scheme of source provinces
1- metamorphic rocks; 2 - granitoids; 3 - clay and marl; 4 - volcano-sedimentary rocks; 5 - flysch; 6 - limestone; 7- clay and sand; 8 -loess; 9 - boundaries of the watershed; 10 - boundaries of the shelf; 11 - rubble-sandy deposit; 12-sandstone. I - Moesian Platform; II - Lower Kamchiya Depression; III - East Stara Planina Zone; IV - Sredna Gora Zone

In many places along the shoreline, such as in the villages of Saraphovo and Aheloj, the magnetite is the most common mineral. The content of this mineral range from 1444 kg/m^3 in the beach sand near the Saraphovo village, and 1972 kg/m^3 near the Aheloj village to reach 975 kg/m^3 in the submarine coastal slope at 3-5 m deep. In some other locations, such as near the cities of Pomorie and Sozopol, the content is less than 1 kg/m^3 (Tzvetanova-Goleva, 1974). A highest content of ilmenite (11-16%) is observed in the south of the Burgas cape. Maximum contents of sphene (7-14%) occur near the Chernomoretz village. The mineral composition of the heavy fraction of beach sands from the southern source province indicates a derivation of material from source rocks of different genesis. The primary sources of magnetite and of most other heavy minerals are the volcano-sedimentary and various igneous rocks, cropping out widely in the Burgas depression (Figure 1).

TABLE 1. Water and solid discharges of the rivers into the Black Sea

No	RIVER	LENGTH km	WATERSHED, km^2	SOLID DISCHARGE 10^3 t/year	WATER QUANTITY m^3/s
1	Batova	38.7	338.8	35.4	0.73
2	Kranevska	13.9	84.5	8.0	0.36
3	Kamchia	244.5	5357.6	462.0	19.25
4	Shkorpilovska	26.9	78.7	7.5	0.34
5	Panairdere	14.9	58.2	5.5	0.25
6	Dvojnitza	52.5	478.8	45.5	2.06
7	Vaja	10.3	40.4	3.8	0.17
8	Drashtela	12.2	38.1	3.6	0.16
9	Hadjiska	55.3	355.8	33.8	1.53
10	Aheloy	39.9	141.0	13.4	0.61
11	Marinka	10.5	30.8	2.9	0.13
12	Otmanly	7.0	19.0	1.8	0.08
13	Ropotamo	48.5	248.7	23.6	1.17
14	Dyavolska	26.9	133.2	12.7	0.57
15	Karaagatch	30.5	224.3	21.3	0.96
16	Lisovo dere	11.2	25.9	2.5	0.11
17	Veleka	147.0	994.8	77.9	8.76
18	Silistar	12.7	21.2	2.0	0.09
19	Rezovska	112.0	183.4	17.4	0.79
	Total			780.6	38.12

TABLE 2. Abraded material of Bulgarian Black Sea coast

No	ABRASIVE AREA	LENGTH km	MEAN VELOCITY OF ABRASION m/year	ABRADED AREA m^2/year	ABRADED VOLUME m^3/year	MASS 10^3t/year
1	c. Sivriborun -c. Shabla	12.5	0.30	3796	42068	61.0
2	c.Shabla-c.Kaliakra	25.8	0.05	1290	22446	56.6
3	c.Kaliakra – Kavarna	11.0	0.05	550	9460	23.8
4	Kavarna-KR Albena	18.3	0.15	2745	45018	90.0
5	KR Albena-c. St. George	6.6	0.15	990	6534	12.7
6	c.St George-C.Galata	3.5	0.20	700	11760	24.2
7	c. Galata-c.Emine	29.5	0.12	3540	50268	103.6
8	c.Emine-Nessebar	12.8	0.08	1024	17613	28.5
9	Nessebar-Pomorie	8.0	0.09	720	5976	12.4
10	Pomorie-c.Foross	9.8	1.05	10290	81291	131.7
11	c. Foross-Rezovska river	99.0	0.01	990	10989	30.8
	General	296.8	0.11	26635	304423	575.3

There is practically no erosion in the igneous rocks; they have no special significance as an independent source of terrigenous material. On the other hand, the volcano-sedimentary rocks, Sarmatian sandstone and limestone, and the secondary collectors of heavy minerals, the Pliocene and Quaternary clays and sands, are more subject to intensive wave erosion. To a large extent, the lithology of the rocks reveals the complicated configuration of the coastline. The landslides developing here accelerate the erosion processes. Investigations on erosion rates carried out in the village of Sarafovo show that the volume of material resulting from the coastal destruction, varies from 2.3 to 23.5 m^3/year (Shuiski and Dimeonova, 1976). Thus, on account of the erosion, about 400t of magnetite are introduced annually into the sea. During the last 3,000 years, the total quantity has reached 1,200,000 t (Khrischev, 1978).

Although the river network of the southern source province is dense, the watershed area is insignificant (Figure 1). The amounts of terrigenous material delivered by river flow and erosion are comparable. Moreover, the modern river mouths are submerged (Tables 1 and 2). A considerable concentration of heavy minerals is noted at the mouth of the Shelly River. The composition of the sediments shows that heavy mineral accumulations are the result of wave reworking of alluvial material supplied by the Aheloy River. The riverbed material of the Aheloy River channel is traced at 5 km from the coast (Khrischev, 1978).

In the process of wave reworking, beach sands in some sectors have been enriched in heavy minerals, more particularly in magnetite. The composition of the heavy-mineral fraction is determined by the lithological composition of the source rocks. The high diversity of rock types, the dense river network and the intensive erosion of beaches in the southern souce province cannot compensate the actual deficit of terrigenous material in the coastal zone.

The Central Source Province

This province is located between the capes of Emine and Varna Bay eastward, the Trans-Balkan deep faults southward, and the Varna lowland northward (Figure 1). The folds of the eastern Balkans can be traced at the seaside. The Low-Kamtchja River depression is a transitional tectonic zone between the Alpine system of the East Stara Planina Mountain and the Misian plate.

Upper Cretaceous to Paleocene sedimentary rocks - represented by an alternation of limestone and quartz sandstone with clayey-calcareous sandstone and clayey limestone - constitute the lithological structure of the province. The Emine flysch, presented mainly by clayey-limy sandstone and clayey-sandy limestone is typical of the region. Sediments of Paleocene (Eocene) and Neogene (Chokrakian, Karaganian, and Konkian) are constituted by sandstone, sandy-clayey limestone and limestone facies in the Varna depression. The Sands of the Dikilitash horizon are predominant and easily destroyed and transported. These sands consist mainly of quartz with some isolated grains of magnetite, hematite and rutile.

The large river valleys (Kamtchija, Funducklijska, Dvojnitza) are refilled with Quaternary alluvium of significant thickness. The granulated fluvial-riverbed deposits of various grain-size and red colors are disposed on both sides of the Kamtchja River channel. These deposits are unconsolidated, fragile and well rounded, and are formed by alluvial material transported by the Kamtchja River during a lower water level of the Black Sea during the Lower Pleistocene. The Kamtchija River valley has a considerably wide water-catchment area and pass through a thick sediment cover. These features cause the delivery by this river of about 1.2. 10^6 t of material per annum into the sea. Recently, this amount has decreased by about three fold because of the construction of irrigation canals (Table 1).

The beaches of the central source province are formed near the mouths of the big rivers, Kamtchija, Funduklijska, Dvojnitza. Terrigenius, weakly carbonate-cemented (up to 8% $CaCO_3$) sandstone crop out in the section between the rivers Kamtchija and Funducklijska. The contents of heavy minerals in the fine-sand sub-fraction are less than 1% in the submarine coastal slope sands and 6% in the beach sands. The sands consist predominantly of quartz (60-70%) with some feldspar (10-15%), rock fragments (15-20%) and the accessory minerals (5-6%). They also contain various amounts of biotite, muscovite, chlorite, tourmaline, garnet, magnetite and others. Quartz, feldspar and rock fragments predominate more in the medium and coarse sub-fractions.

South from the Cape of St Athanas, the heavy minerals from coarse-aleurite (silt) subfraction are represented by magnetite (59%) and pyroxene (26%). The light fraction consists mainly of quartz (average: 41.9%) with some feldspar, rock fragments and detritus.

The mineralogical composition of the beach and submarine coastal slope sediments reflects the composition of the primary rocks in the source province. The sedimentary material brought to the sea is provided by the solid discharge of the Kamtchija, Funducklijska and Dvojnitza rivers and ephemeral streams as well as coastal erosion. These material participate in the formation of wide beaches and sediment accumulation in the submarine coastal slope opposite to of the river mouths. The central source province, as well as the southern one, is now characterized by a deficiency of sedimentary material.

The Northern Source Province

This province covers the northern part of the Moesian plate. It is delimited in the south by the latitude crossing the Varna Bay and in the north by the Romania frontier (Figure 1). The lithological structure of the province is rather uniform. The Neogene carbonate complex, Pleistocene loess and indurate loess in the north are the predominant rocks. The Sarmatian Complex is represented mainly by an alternation of limestone, silty clays and clayey sandstone. The Lower-Middle Sarmatian sedimentary rocks generally overlie the Oligocene clays that cause active landslides in this area. The beach sands are product of the erosion, mainly as regards quartz sandstone, in the Upper Sarmatian and Chokrakian sandstones and the loess sediments on the northern coast.

The beach sands are also due to erosion, whereas sands on the submarine coastal slope are evidently under the influence of the solid discharge from the river Danube (Rojdestvenski, 1972). Mineralogical investigations of the beach sands show the presence of 32 minerals in the heavy fraction and 8 minerals in the light fraction. In some samples, the heavy mineral content in the 0.25 - 0.10 mm subfraction reaches up to 28-35% of the sediment. Most frequently, the beach sands are composed mainly of quartz and carbonate shell material. The content of carbonates varies from 50% (Albena resort) to 95% north of the Albena resort and consists mainly of biogenic components.

The high concentrations of heavy minerals are located near the rivers mouth. The heavy-mineral fraction is composed mainly of epidote, magnetite, diopside and garnet with some common zircon, sphene and amphibole (Tzvetkova-Goleva 1975). The low roundness of the rock forming the mineral grains; the presence of fresh and angular epidote, sphene, pyroxene, olivine and graphite indicate the close proximity of the source province.

At the present time, the main sources of terrigenous material on the shelf in the west and northwest of the Black Sea are the Danube and Dnester rivers, which wide water catchment areas. Regardless of the fact that they deposit part of their sediment load in large firths, they import annually into the sea about 88,100,000t of solid material, consisting mainly composed of silicate with only about 250,000t carbonate (Shimkus and Trimonis, 1974). The Danube river is the largest transporting agent of solids with 830,000,000t (Bol'shakov, 1970).

The present circulation scheme of the water masses on the shelf suggests an increase in the material delivered by the above-mentioned rivers (Danube, Dnieper) and its sedimentation into the central shelf area. This is supported by the high sediment accumulation rates, exceeding 5-m/ kyr. The annual solid discharge from the source provinces of the western Black Sea (Tables 1, 2) is 60 times less than the solid discharge of the Danube. More than half of the Danube load is represented by coarse and fine aleurite (silt) material while the remaining part is constituted by clay-size (Trimonis, 1975). This, together with the present surface circulation pattern, causes the highest density suspensions (up to 10 mg/l) on the shelf where the Danube waters predominate. These waters are found at 20-30 km at the east of the river mouth and extends southwards, covering the central part of the shelf. The surface currents of the western shelf form anti-cyclonic cells in the Varna and Burgas bays, where accumulation swells are produced.

At the time of strong north and northeast winds on the western shelf, not only strong surface currents with velocities of 1.3-1.5 m/s occur, but also bottom currents of up to 1.3 m/s velocities at 20 to 50 m of depth, in the southern and northern directions are observed. On the periphery of the shelf, the currents have lower velocities (0.2-0.7 m/s). These currents can transport grains of gravel size and wash away clay, sand and silt size material from the bottom sediments. (Longinov, 1973). According to the Hjulström curve, the clay, silt, sand and gravel fractions can be removed by currents with velocities of 0.5, 0.2-1.5 , 0.15- 0.30, and 0.2-1.5 m/s, respectively. These values are valid only for sediment following a "unimodal"size distribution. The wash away speeds for sediments with "polymodal" size distribution are defined by the largest size fraction. In the case of an insignificant addition of clay material to sediment sharply increases the velocities required for removal, whereas the addition of insignificant quantities of coarse-grained material to a clay-size sediment sharply decreases the removal velocities.

During times of continuous southerly, southwesterly and westerly winds, strong coastward-flowing compensation currents occur in order to counterbalance the surface currents formed by the wind effect. For short periods, these compensation currents transport sedimentary material and the deep-water hydrogen sulfide-bearing waters on the shelf towards the coast.

CONCLUSIONS

The following conclusions can be reached regarding the main sources of sediment material delivered to the western shelf and the processes operating in different parts of western coast:

(1) The erosion of sedimentary material from the land area is characterized by the formation of typical thin weathering crusts and predominant mechanical weathering under the conditions of a moderately humid climate.

(2) The land area constituting the source of the sedimentary material is heterogeneous in terms of its structure and the composition of geological formations. It can be divided into three distinct source provinces. The sedimentary material is delivered to the sea by the rivers and ephemeral streams, and by the erosion and abrasion of the slopes and coasts. The main source of terrigenous material deposited on the shelf is the watershed areas of the rivers; this source provides about 100 times more sediment material than the other sources, such as the coastal and slope abrasion and erosion.

(3) The three source provinces have been defined by the chemical, mineralogical and granulometric composition of sandy beech deposits and submarine coastal slope sediments. In the southern source province these sediments are characterized by a sharp increase in the amount of the heavy-mineral fraction, in the central source province by the predominance quartz sands and in the northern source province by high carbonate contents. The specificity of material and mineralogical composition of beach and submarine coastal slope sediments reflect the characteristics of the source provinces on adjoining land.

(4) The modern epoch is characterized by a deficit of terrigenous material, which enter the shelf from source provinces and are distributed under influence of various hydrodynamic factors.

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WATER AND SEDIMENT TRANSPORT BY THE DANUBE INTO THE BLACK SEA DURING 1840-1995

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ABSTRACT

This paper shows the results of the numerical analyses of long time series of data regarding the annual water and sediment discharges of the Danube into the Black Sea, during the period between 1840 and 1995. The computed parameters include the annual characteristic values (maximum, average, minimum), statistical parameters (standard deviation, coefficient of variation and coefficient of skew) and time trend of water and sediment inputs, based on long time series of data.

During 1840-1995, the transport of water and sediment from the Danube to the inlet of the Black Sea, was evaluated at water discharge mean rate of 6238.5 m^3/s (196.9 km^3/yr) and at a mean sediment discharge of 1713.1 kg/s (54.061325 million t/yr). The time variation of the water discharge shows a linear trend increasing at a rate of 2.84 $m^3/s/yr$, whereas the time variation of the sediment discharge displays a curved exponential decrease at a rate of about 8.5 kg/s/yr.

INTRODUCTION

Hydrological and hydrographic observations and measurements have been performed in the fluvial and littoral zone of Romania for more than 160 years (Hartley, 1862; Rosseti.and Francis, 1931). The data accumulated in the last century by navigation organizations and the former administration of the Turkish Ottoman Empire in the Danube Delta and by the former Austro-Hungarian Empire on the Danube were archived by the Romanian State under the care of the National Hydrological Service. At present this data bank is managed and utilized in a unitary way by the National Institute of Meteorology and Hydrology of Romania. It has been updated with new hydrological and oceanographic data accumulated by the Romanian State, in collaboration with specialized organizations from Russia and Ukraine (Diaconu et al., 1963).

Processing and analysis of these data by the Hydrological Service of Romania provided a new insight into the past and present hydrological regime of the Danube - the Black Sea beginning with the first half of the last century (Bondar , et al, 1973; Diaconu et al., 1963; Stanescu et al., 1967). These studies also considerably improved our knowledge on the hydrological regime of the neighboring coastal zone in terms of water and sediments run-off, salt and biomass thermal phenomena, the waves and currents, coastal water and sediments circulation, as well as the morphological littoral processes. The Romanian Hydrological Service published the results of these studies in three important hydrological monographs in the post-world war period (1963). These monographs cover the Danube Delta (1963), the Romanian border sector of the Danube (1967) and the Romanian coastal zone of the Black Sea (1973). Lately, other more specific monographs on the water and sediment run-off of the whole Danube basin have been published.(Rakoczi et al., 1993; Stancik and Jovannovic, 1988),

In this paper, we present some results of the studies carried out by the National Hydrological Service on the annual water and sediment discharges into the Black Sea at the Danube's mouths.

THE DANUBE WATER RUN-OFF INTO THE BLACK SEA

The aquatic environment of the Black Sea is closely influenced by the continental water inputs. In the western part of the Black Sea, 79% of the total volume of continental waters is delivered by the Don, Nipru, Bug, Nistru and Danube rivers. The Danube contributes more than 60% of this total.

The chronological graph of the Danube's regime of mean annual water discharge shows a linear regression trend between 1840-1995 (Figure 1). Table 1 presents the statistical parameters related to the water discharge and its time series evolution corresponding to numerical temporal values.

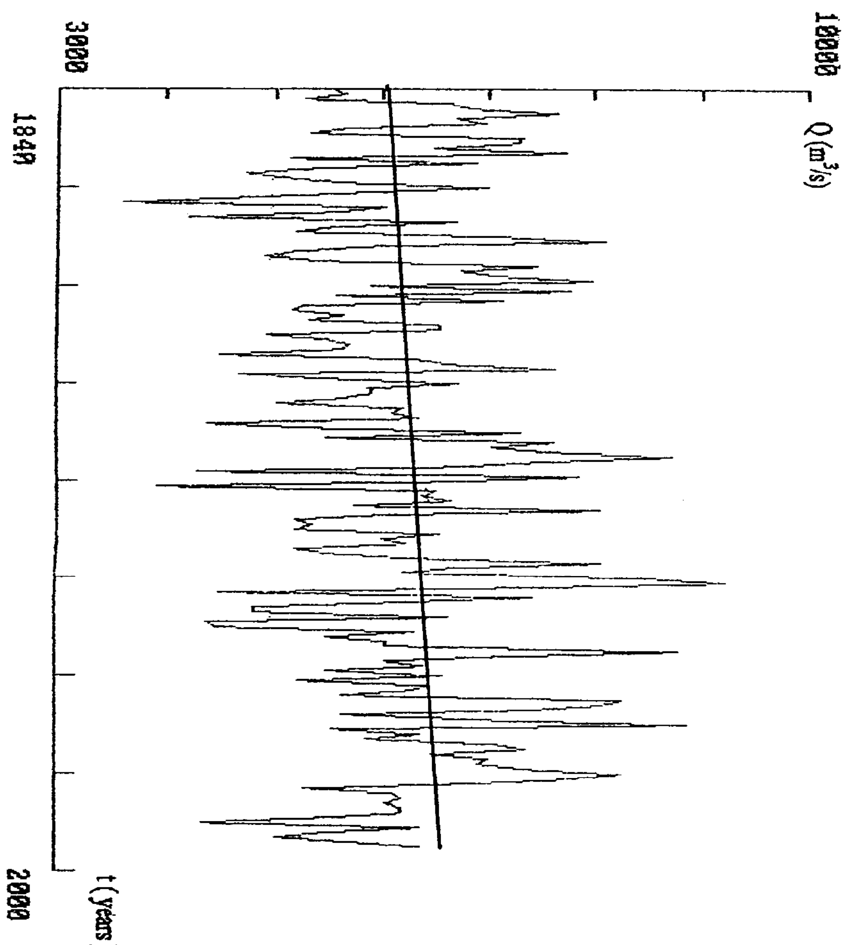

FIGURE 1. Chronological graph of mean annual water discharge and linear regression trend from 1840 to 1995.

TABLE 1. Statistical parameters of trend and of oscillation of the mean annual Danube's water discharges to the Black Sea during the period 1840-1995 time

Parameters	Numerical values
1. Maximum (m^3/s)	9250.3
2. Maximum year	1941
3. Multiannual mean (m^3/s)	6238.5
4. Minimum (m^3/s)	3614.2
5. Minimum year	1863
6. Standard deviation	1091.9
7. Variation coefficient	0.175
8. Asymmetry coefficient	0.289
9. Linear trend coefficient	2.84
10. Mean oscillation period	31
11. Mean oscillation amplitude	456.4
12. Initial phase	5.896

From the analysis of Figure 1 and Table 1, the following characteristics of the Danube annual water input to the Black Sea from 1840 to1995 can be discerned:

- the water secular inflow is characterized by a multi-annual water discharge of 6238.5 m^3/s (196.9 km3/yr);
- the mean annual water discharges varied between 9250 m^3/s in 1941 and 3614 m^3/s in 1863; the
- standard deviation is about 1092 m^3/s ;
- the variation coefficient and asymmetry coefficient of time oscillation are 0.175 and 0.289 respectively;
- the mean time variation period of the mean annual water discharges is 31 years, with an amplitude of about 456 m^3/s. The time period of large and small run-off of the Danube is repeated every 31 years.

The important volume of water delivered by the Danube to the Black Sea produces annual variations of the water level, with effects on water and salt balances. Under these circumstances, it is necessary to perform a research on water and salt balances involving the whole river countries. Such a study could be carried out in co-operation with the countries of the Danube in the framework of an International Hydrological Programme.

THE DANUBE SEDIMENT RUN-OFF IN THE BLACK SEA.

The Danube water flow brings large amounts of sediments into the Black Sea. It delivers an annual sediment discharge of 54,000,000 t (84% of the total river sediment input) consisting of silt, clay and sand, with a grain size of up to 1.5 mm.

Figure 2 shows the chronological graph of the mean annual discharge of sediment from the Danube into the Black Sea, and its trend from 1840 to 1995. The graphs indicate an oscillatory variation in time of the annual mean sediment discharge of the Danube and its decreasing time trend. Statistical parameters of the annual sediment run-off are given in Table 2.

Examining Figure 2 and Table 2, the following characteristics of annual sediment inflows of the Danube in the Black Sea during 1840-1995 arise:

- the sediment secular inflow is characterized by a multi-annual sediment discharge of 1713.1 kg/s (54.06 10^6 t /yr);
- the annual mean sediment discharge varied between 4470 kg/s in 1871 and 229 kg/s in 1990;
- the standard deviation is about 794 kg /s ;

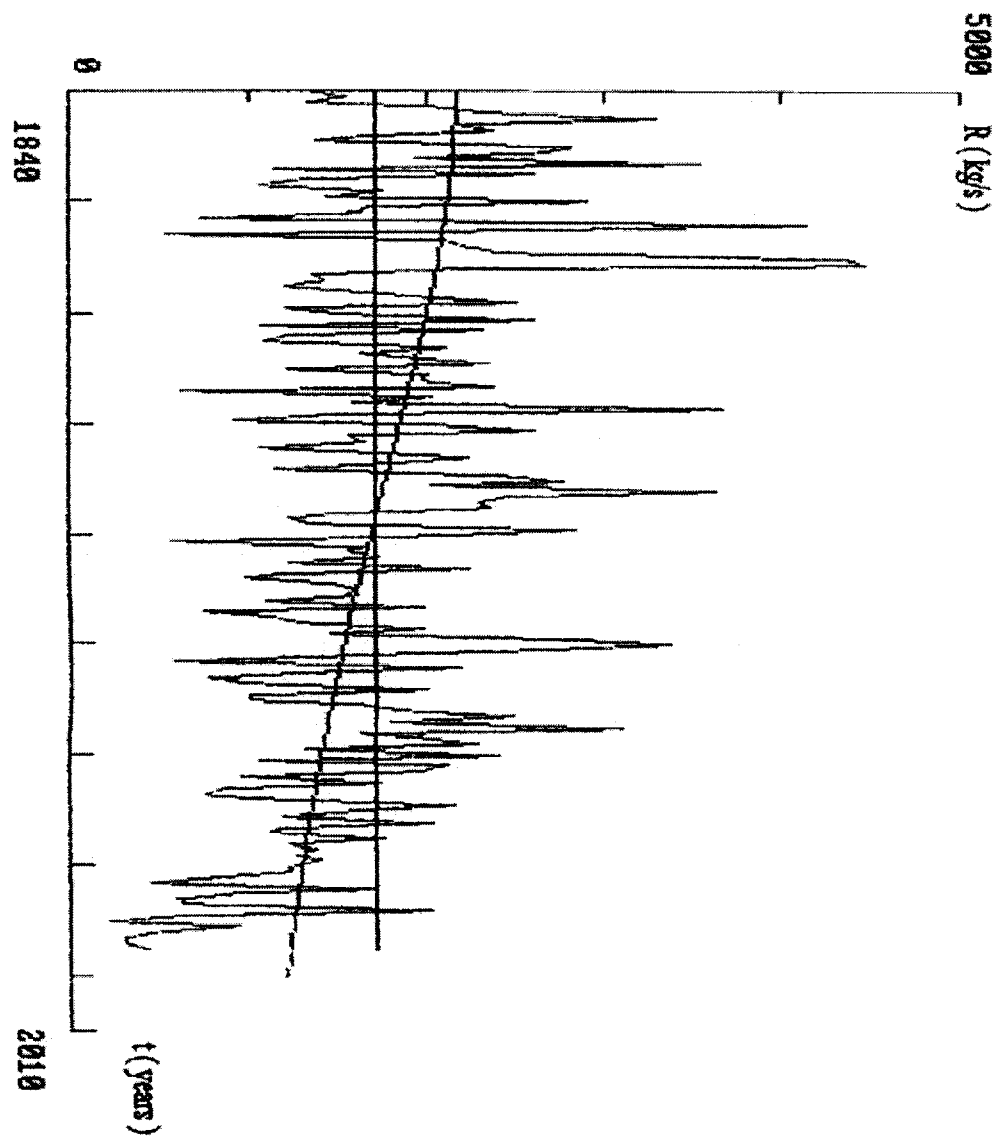

FIGURE 2. Chronological graph of mean annual Danube's sediment discharge and the trend graph on 1840 - 1995 years.

- the coefficients of variation and asymmetry of time oscillation are 0,464 and 0,838, respectively.
- the mean time variation period of the annual mean sediment discharge is 22 years, with an amplitude of about 340 kg/s.

The time period with large and small sediment run-off from the Danube is repeated every 22 years.

During the last three decades, the sediment run-off of the Danube decreased constantly in time, due to natural and man-made causes. The man-made causes led to a reduction in sediment supply, due to the construction of an important embankment and hydrotechnical works on the course of the Danube and its main tributaries. As a consequence of the dam building on the riverbeds, there has also been a decrease of the sediment discharge to the Black Sea from the Danube hydrographic basin.

The variation in the large volume of sediments delivered by the Danube to the Black Sea has in turn produced some annual oscillations in the distribution of the sediments in the littoral zone, with effects on the littoral (coastal) morphological balance and sea water transparency. The decreasing trend sandy sediments input of the Danube into the Black Sea had negative effects on beaches, causing a predominant process of erosion. Following this process, the grain-size distribution and the mineral composition of the beaches were radically changed, due to the increase of the organogenic composition of sand, due to the presence of broken marine shells and snails.

TABLE 2. Statistical parameters of trend and of oscillation of the annual mean sediment discharges of the Danube into the Black Sea during the period 1840-1995

Parameters	Numerical values
1. Maximum (kg/s)	4470.2
2. Maximum year	1871
3. Multiannual mean (kg/s)	1713.1
4. Minimum (kg/s)	229.3
5. Minimum year	1990
6. Standard deviation (kg/s)	794.4
7. Variation coefficient	0.464
8. Asymmetry coefficient	0.838
9. Linear trend coefficient	-6.94
10. Mean oscillation period (years)	22
11. Mean oscillation amplitude (kg/s)	340
12. Initial phase (rad)	5.33

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INPUT OF POLLUTANTS FROM THE DANUBE IN THE SEDIMENTS ALONG THE ROMANIAN COAST OF THE BLACK SEA

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ABSTRACT

This paper presents the results of studies carried out at the Romanian Marine Research Institute (RMRI), Constantza, aiming at the identification of pollutants, such as heavy metals, hydrocarbons, radionuclides and nutrients, in the sediments collected from the coastal area of the Romanian Black Sea shelf. The data show that the degree of contamination in the marine area off the Danube mouth is influenced by the association of hydroclimatic factors with the inputs of terrigenous and anthropogenic origins, which characterize each investigated area.

INTRODUCTION

The continental anthropogenic pressures induced by the affluent rivers and coastal economic activities directly influence the Romanian coastal marine area. The RMRI Constantza carried out a monitoring programme based on the measurement of the main physico-chemical quality parameters of the coastal waters, and of ecosystem conditions. Within the framework of this programme, special attention was paid to the identification and measurement of pollutants delivered by the Danube into the near-shore shelf of the Romanian Black Sea.

This paper shows the results of the studies involving analyses of metals, total hydrocarbons, radionuclides and nutrients in the sediments collected from five profiles near the Danube mouth (Figure 1). These profiles are located vertically to the coast off Sulina, Mila 9, Sfantu, Gheorghe, Portita and Gura Buhaz.

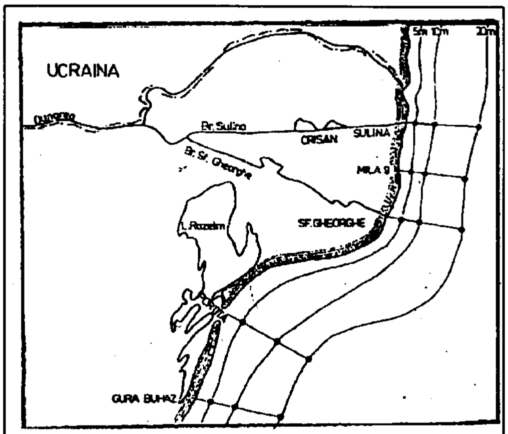

FIGURE 1 Sampling location of the sediments in the Pre-Danubian sector of the Black Sea in 1996

SAMPLING AND ANALYSES

For the heavy metal and hydrocarbon studies, the sediments were collected from 5, 10, and 20 m isobaths and, as regards radionuclide analyses, from depths ranging between 14 and 82 m, corresponding to 7 and 10 nautical miles from the shoreline, on the same profiles. A van Veen type grab sampler was used for the sampling.

Cd, Pb, and Cu in the surface sediments were analyzed using an Ati-Unicam Solaris 939, model Atomic Absorption Spectrophotometer with Zeman correction device (UNEP, 1982, 1983).

The total hydrocarbon content in the sediments has been measured by means of a UV spectrum detection method, using a Hewlett Packard 8453 spectrophotometer. A method recommended by the Workshop on Sampling and Analysis Methods for Oil Pollution Monitoring in the Aquatic Environment, held in Budapest in 1994, was used for the preparation and analysis of samples. For calibration of samples the *"Danube Reference Oil"* was used as standard oil type (UNESCO,1984).

The total beta activity measurements were calibrated with a ^{40}K standard. ^{90} Sr was dosed through radiochemical separation in the presence of a carrier (IAEA,1989; Harvey et al, 1989; IISP,1994; EPA,1984). The measurement of the total beta radioactivity and beta radiation of ^{90}Y was carried out with a specific low-level radiometric equipment. The gamma spectrometric analyses were carried out on a high-resolution device, and an international intercalibration process organized by IAEA controlled the results. The nutrient analyses were made according to the UNEP (1988) method

RESULTS

Heavy Metals

The content and distribution of heavy metals in the sediments collected during 1996 (Table 1; Figs. 1 to 5) indicate a southward decreasing tendency of heavy metal contents along the 10 m isobath. At the southern limit of the studied zone, the Pb content of the samples collected at the Gura Buhaz station, was reduced by 4 fold and Cu by 6.5 fold, compared with those of samples collected at the Sulina branch mouth.

TABLE 1 Metal contents of the sediments (Mihnea and Pecheanu, 1996)

Element	Range (µg/g)
Cu	1 – 14
Pb	40. – 590
Cd	1.19 - 4.55

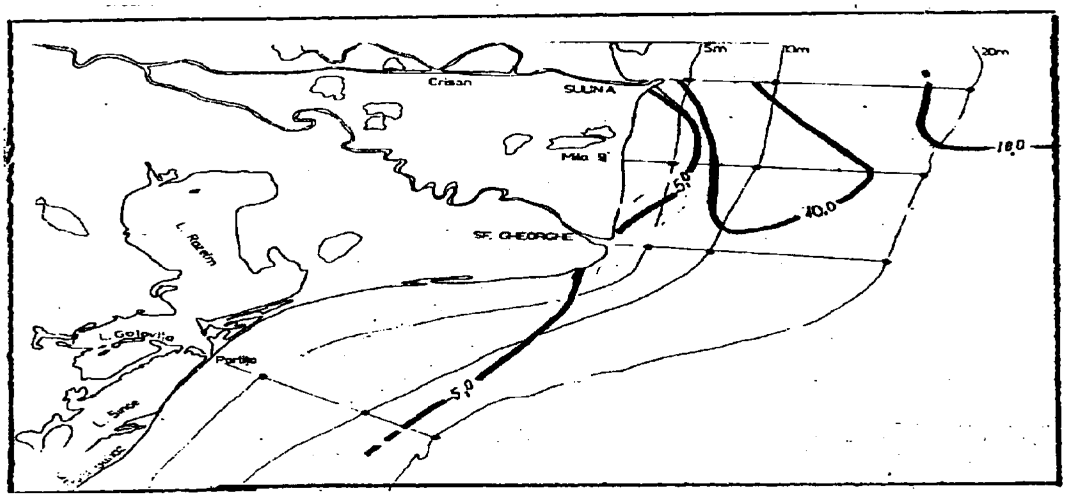

FIGURE 2. Distribution of Cu (µg/g) in sediments collected in 1996

The generally higher contents of heavy metals in samples located on the 20 m isobath compared with those of samples located on 10 m isobath are mainly due to the finer grain size of the former samples, and to a lesser extent to the result of pollutant accumulation because of the hydrometeorological conditions specific for that zone affected predominantly by northeasterly winds and sea currents (Figs. 2 to 6; Table 2).

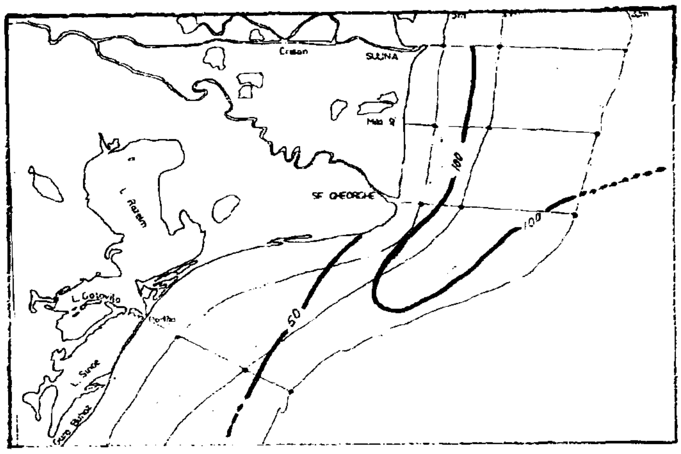

FIGURE 3. Distribution of Pb (μg/g) in sediments collected in 1996

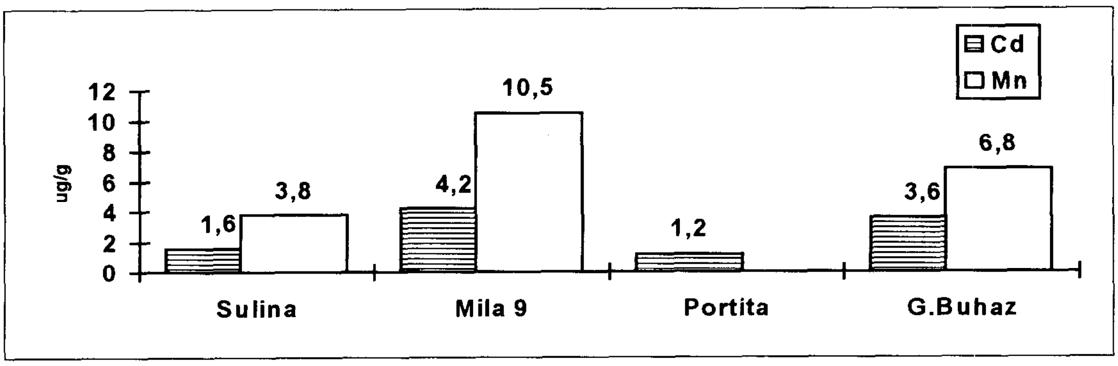

Figure 4. Spatial distribution of Cd and Cu (μg/g) in sediments collected from 10-m isobath in the pre-Danubian sector in 1996.

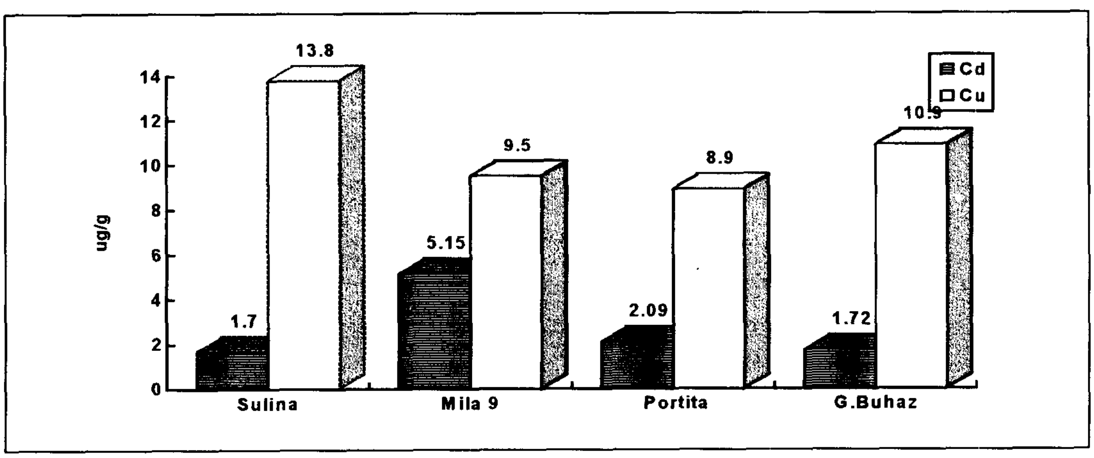

FIGURE 5. Spatial distribution of Cd and Cu (μg/g) in sediments collected from 20 m isobath in the pre-Danubian sector in 1996

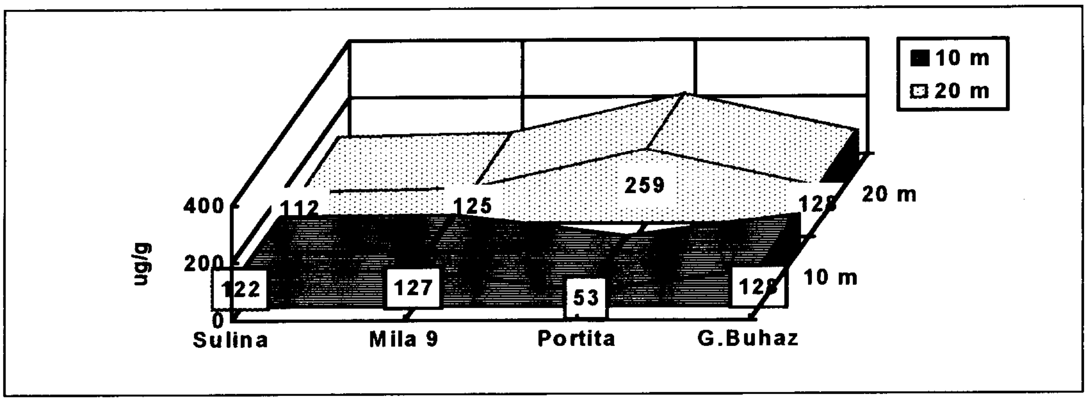

FIGURE 6. Spatial distribution of Pb (μg/g) in sediments collected from the 10-m and 20 m isobaths in the pre-Danubian sector in 1996

TABLE 2. Differences between the heavy metal contents of sediments collected on 10 and 20 m isobaths (%)

Profile	Cd	Cu	Pb
SULINA	+ 30	+ 51.6	+ 8
MILA 9	+ 14.4	- 29.1	+ 1.6
PORTITA	+ 75.6	+ 16.9	
GURA BUHAZ	- 46	+ 678.5	+ 357

Hydrocarbons

The investigation concerning the evolution of oil pollution off the Danube mouths is based on the comparative analysis of the amplitude and dynamics of this phenomenon related to the characteristics of the pollution contribution from land-based sources. The degree of oil contamination has been established through two investigations:

- Determination of the oil pollution load of the Danube waters at the point of discharge into the marine environment, at the Sulina channel.

- Determination of the oil content of water and sediment samples collected on the 5, 10 and 20 m isobaths between Sulina and Gura Buhaz (Figure 1) (Mihnea and Piescu, 1996).

The analyses of water and sediment samples collected in 1996 have produced high total hydrocarbon contents (Table 3). These high values, with 82 % of the water samples containing between >100 μg/l, and 35.7 %; and of the sediment samples containing >100 μg/g, confirmed the existence of a chronic oil pollution off the Danube mouths.

TABLE 3. Total hydrocarbon content of the water and sediment samples

Zone	Water (μg/l)	Sediments (μg/g)
River zone	303.5	99.07
Sea zone	144.1 - 643.5	23.9 – 265

The spatial distribution of the data shows that, in general, the total petroleum content of sediments and waters decrease from north to south (Table 4; Figs. 7 to 10). The petroleum content of the samples collected on the Gura Buhaz profile in the southern limit of the study area is 3.3 times lower than in the samples collected on the Sulina profile in the north (mean value 181.4 μg/g) (Figure 7). There is a tendency of increased oil pollutant storage in the sediments from the 5-m isobath, as a consequence of the substratum characteristics (Figure 8), with a degree of oil contamination decreasing according to the distance from the coast. Compared with the oil content on the 5 m isobath, it is 2 to 9.4 times lower on the 10 m isobath, and 1.7 to 8.7 times lower on the 20 m isobath (Figures 9 to 11).

TABLE 4. Oil content in the sediments collected from the Danube mouth in 1996 (μg/g)

Isobath (m)	SULINA	MILA 9	SFANTU GHEORGHE	PORTITA	GURA BUHAZ
Channel	99.07	-	-	-	-
5	-	236.8	226.8	114.9	-
10	68.2	25.9	23.9	55.5	51.1
15	211.1	-	-	-	-
20	-	38.3	25.8	67	59.4
25	265.8	-	-	-	-

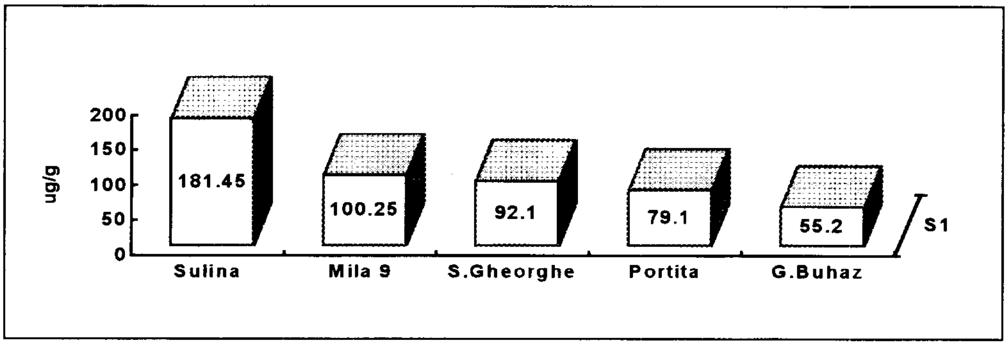

FIGURE 7. Average "total" hydrocarbon contents (μg/g) off sediments collected in the pre-Danubian sector in 1996.

As illustrated in Figure 13, the level of oil contamination in the sediments from all five profiles in the study area has decreased with the time from 1993 to 1996. The river contribution and the cumulative effects of the anthropogenic factors specific for navigation justify the significant petroleum load in the sediments in the Danube mouths area. The results of these studies required further detailed studies, especially on the qualitative analysis and identification of the hydrocarbon components in the biotic sampling media of the marine ecosystem, using GC-MS techniques. Such studies are underway at the RMRI.

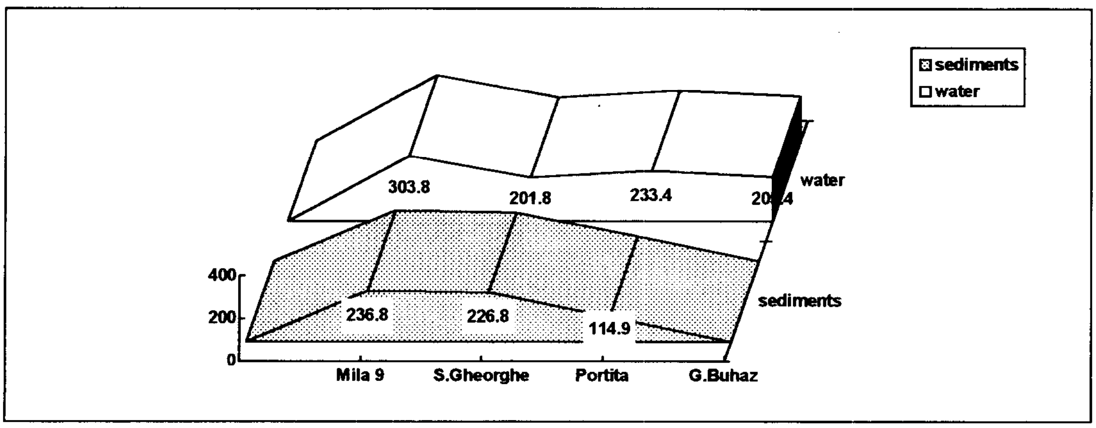

FIGURE 8. Spatial distribution of "total" hydrocarbon content of water (μg/l) sediment (μg/g) samples collected on 5 m isobath in the pre-Danubian sector in 1996

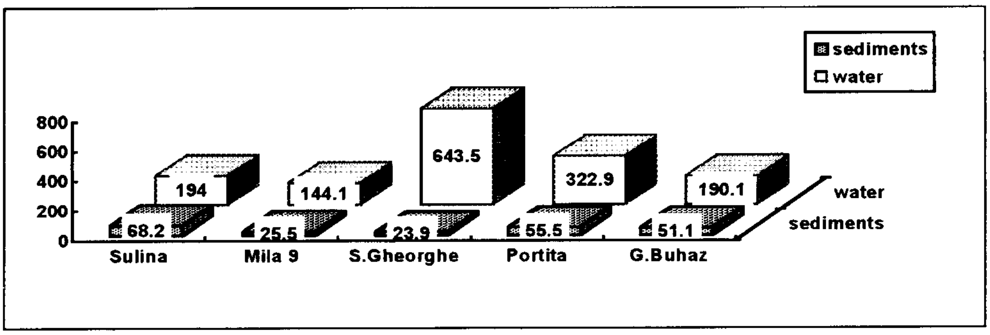

FIGURE 9. Spatial distribution of total hydrocarbon content in the water (μg/l) and in the sediments (μg/g) collected on 10 m isobath in the pre-Danubian sector in 1996

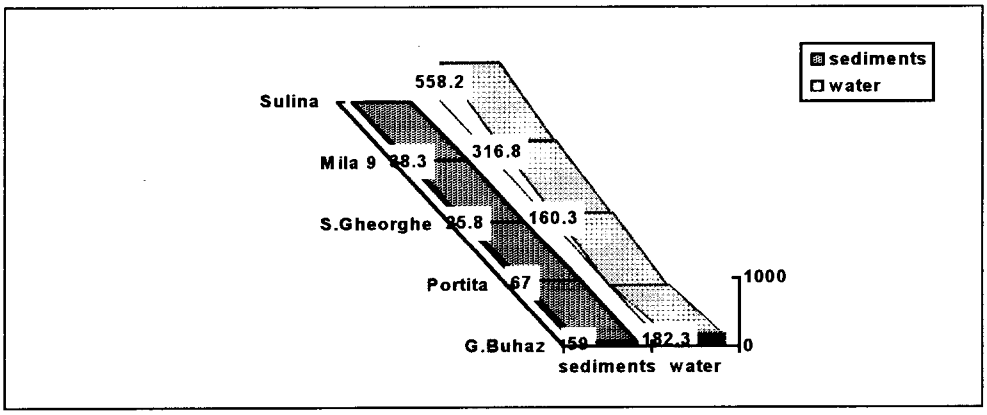

FIGURE 10. Spatial distribution of total hydrocarbon content in water (μg/l) and sediments (μg/g) samples collected on the 20 m isobath in the pre-Danubian sector in 1996

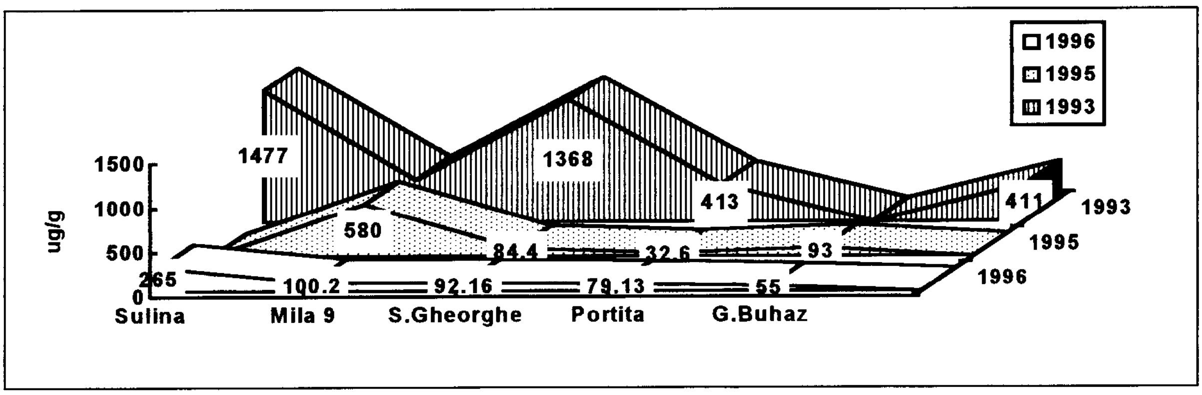

FIGURE 11. Average "total" hydrocarbon content (μg/g) of sediments collected in the preDanubian sector in 1993 - 1996

Radionuclides

The monitoring of marine radioactivity along the Romanian coast of the Black Sea has been systematically carried out by the RMRI. These natural and artificial radioactivity studies involved the total beta radioactivity, ^{90}Sr beta radiometric and gamma spectrometric measurements. In 1996, 81% of the sediments periodically collected in the Danube mouth area represented a significant high total beta activity (Mihnea et al., 1996).

Total beta activities higher than 800 Bq.kg^{-1} d.w. have been registered on the Mila 9 and Portita profiles located under the influence of the Danube branches of Sulina and Sfantu Gheorghe (Table 5). The major contribution of the Sfantu Gheorghe branch is shown by a maximum value of 765 Bq.kg^{-1} d.w. measured on the profile at this station. The fluctuations in the dynamics of the total beta activity of the surface sediments are caused to a great extent by hydrological factors determining the size and density of the settling particles. This explains why more intensive activities have been observed at higher depths of the marine environment, than those measured close to the river mouths.

In 1996, the total beta activity of the sediments collected during Summer is much higherl compared to the beta activity of sediments collected during Spring and Autumn (Figure 14).

TABLE 5. Total beta radioactivity (Bq.kg^{-1} d.w.) of the sediments collected in the marine area of the Danube mouth in 1996.

Value/Profile	SULINA	MILA 9	SFANTU GHEORGHE	PORTITA	GURA-BUHAZ
Minimum	< 423	< 359	260	< 418	350
Maximum	584	822	765	842	500
Mean	453	528	417	500	410

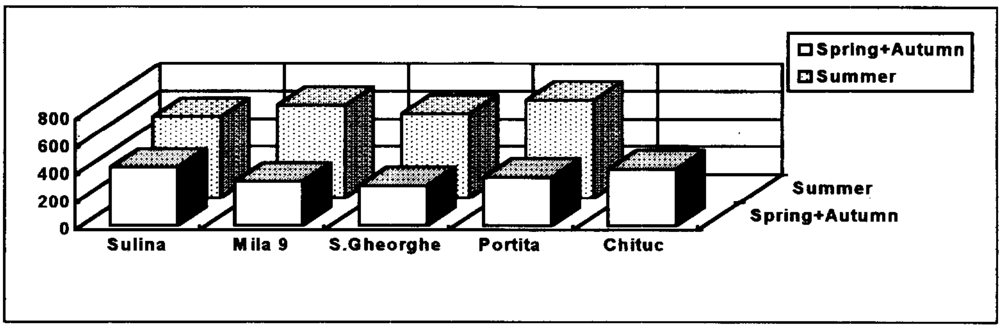

FIGURE 12. Seasonal variation of the total beta radioactivity (Bq.kg^{-1}d.w.) during spring and autumn compared to the summer of 1996

In order to select the sediment samples to be analyzed for ^{90}Sr, an extensive spatial and temporal distribution was carried out, also taking into consideration the total beta activity. All the analyzed samples were characterized by a significant ^{90}Sr radioactivity, between 1.35 Bq.kg^{-1} d.w. at Sfantu Gheorghe in April, and 8.11 Bq.kg^{-1} d.w. at Sulina in July (Table 6).

TABLE 6. ^{90}Sr radioactivity (Bq.kg^{-1} d.w.) of the sediments collected in the Danube mouth area in 1996

Value/Profile	SULINA	MILA 9	SFANTU GHEORGHE	PORTITA	GURA BUHAZ
Minimum	2.46	2.55	1.35	3.29	-
Maximum	8.11	7.07	5.71	3.29	-
Mean	5.30	4.78	3.94	3.29	-

The seasonal dynamics of ^{90}Sr concentrations carried out during April and July are similar to those presented for the total beta activity. The ^{90}Sr Summer values are notably increased: they are on average 2.6 times higher than the Spring values (Fig. 13).

In 1995, the results of ^{137}Cs-gamma spectrometric analysis of the sediments collected in the study area along the 20-m isobath, indicated radioactivity levels between 23 $Bq.kg^{-1}$ d.w. at Mila 9 and 189 $Bq.kg^{-1}$ d.w. at Portita (Mihnea, et al., 1996; Fig. 14). Compared with the previous investigation period between 1994-1995, the results in 1996 show an increase of sediment radioactivity in the Danube mouth area by 26.5-68.4 % for the total beta measurements, and by 42.4-54.5% for ^{90}Sr (Patrascu et al, 1994; Cuingioglu et al., 1996; Figs. 15, 16).

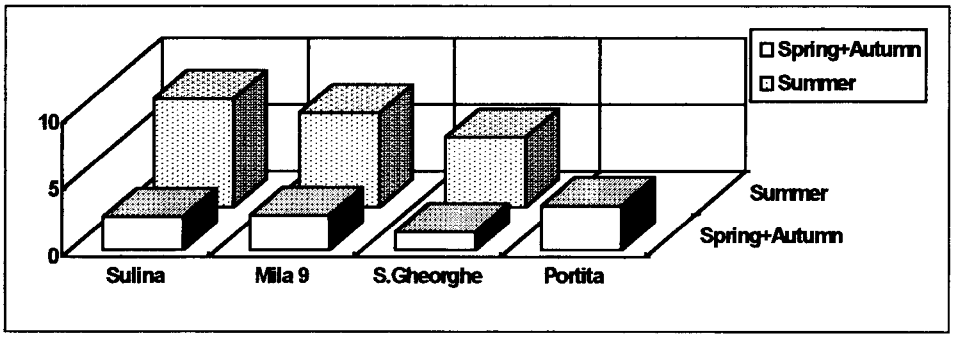

FIGURE 13. Seasonal variations of ^{90}Sr radioactivity ($Bq.kg^{-1}$d.w.) during spring and autumn compared with the summer 1996.

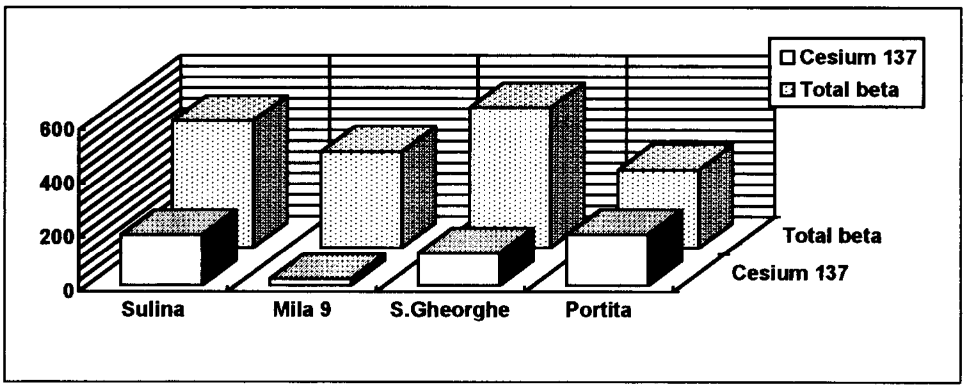

FIGURE 14. Total beta radioactivity and ^{137}Cs activity ($Bq.kg^{-1}$d.w) of the sediments collected from 20-m isobath in 1996

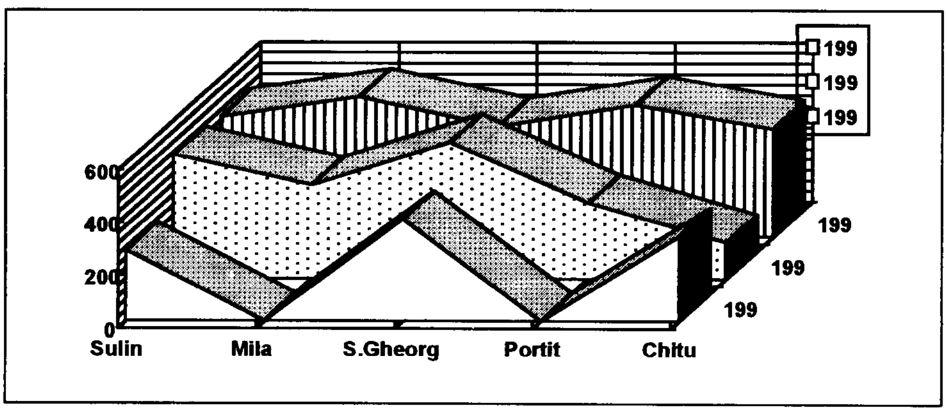

FIGURE 15. Total beta radioactivity (Bq.kg^{-1}d.w.) of sediments (as average values of profile) collected during 1994 – 1996

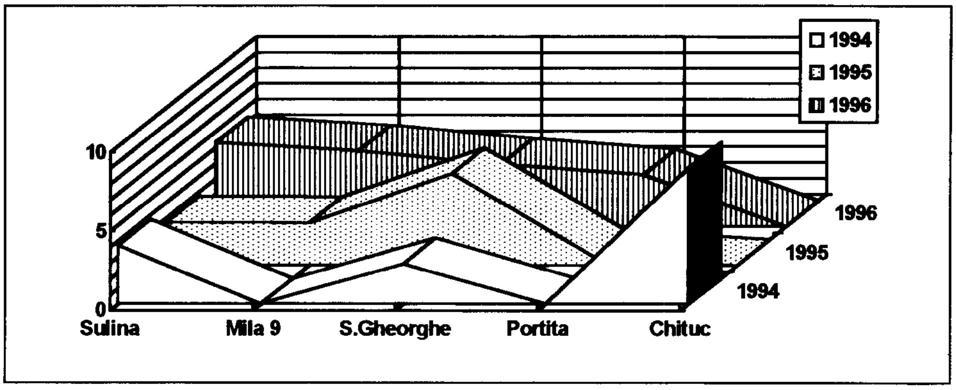

FIGURE 16. ^{90}Sr activity (Bq.kg^{-1}d.w.) of sediments (as average values of profile) collected from 1994 to 1996

Nutrients

The analyses of nutrients in pores of the surface sediments contained in the water collected from the Danube mouth in 1994, are given in Table 7. Along the 10-m and 20 m isobaths studied, there are different levels of nutrients (Figures 17 to 20). In the interstitial waters from the sediments collected on the 10-m isobath at Sulina, Mila 9, and Sfantu Gheorghe in the northern part of the area of study, mean contents of 24.46 µM P-PO4, 113.8 µM Si-SiO4, 407.6µM N-NO3, 6.4 µM N-NO2 and 570.2 µM N-NH4 were determined. The interstitial waters from sediments collected on the 20-m isobath show increases of 89.2% for phosphates, 84.8% for silica, 9.8% for NO_3+NO_2, and 18% for ammonia, in comparison with levels observed on the 10-m isobath. Moreover, the nutrient concentrations are notably reduced in the samples collected in the southern limit of the investigated area, the lowest nutrient contents being identified at the Gura Buhaz station.

TABLE 7. Nutrient content (µM) in pores of sediments contained in waters collected at the Danube mouth (Mihnea and Cociasu, 1996)

P-PO_4	Si-SiO_4	N-NO_3	N-NO_2	N-NH_4
1.7 - 75.4	119 - 310	32.5 - 505.2	0.8 – 19.8	23.3 - 480.3

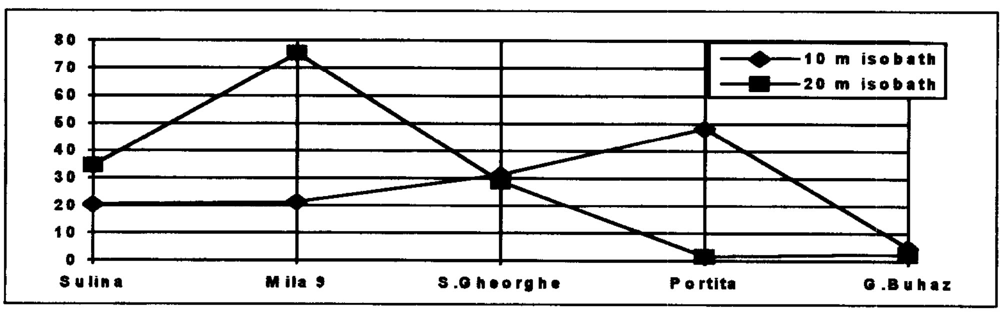

FIGURE 17. Spatial distribution of the average P- PO_4 (µM) contained in sediments from interstitial waters collected at 10 m and 20 m isobaths in 1994

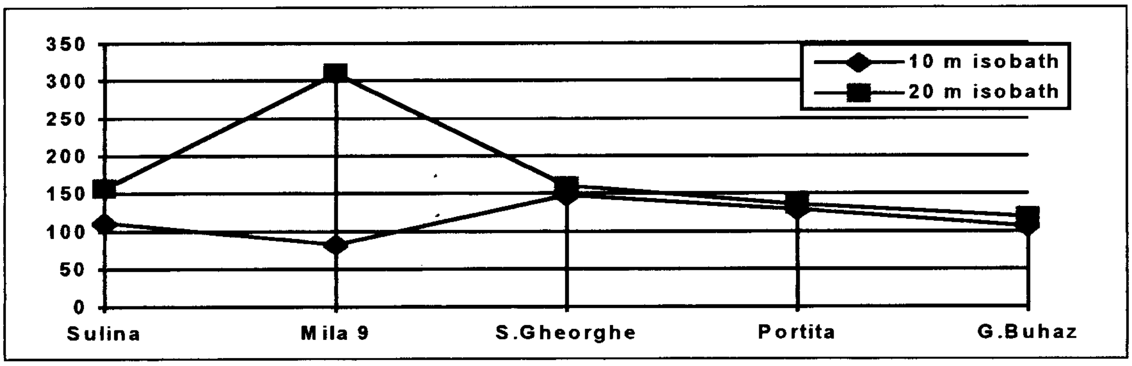

FIGURE 18. Spatial distribution of the average Si-SiO_4 (μM) contained in sediments from interstitial waters collected at 10 m and 20 m isobaths in 1994

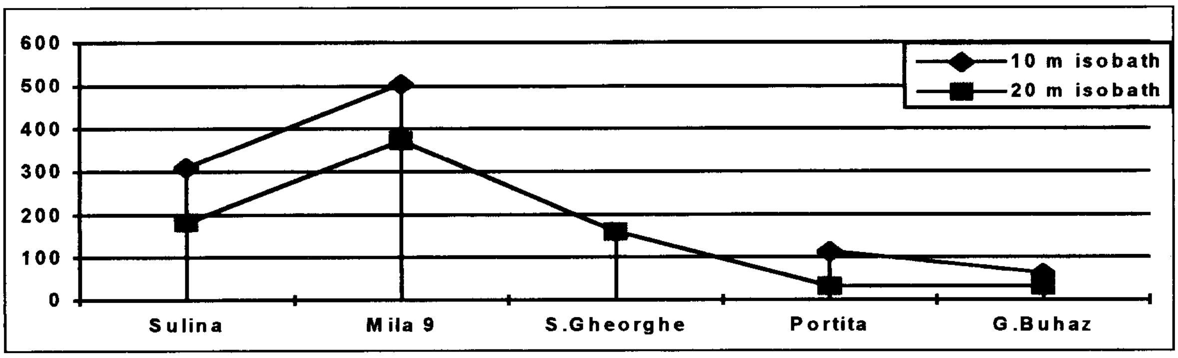

FIGURE 19. Spatial distribution of the average N-NO_3 (μM) contained in sediments from interstitial waters collected at 10 and 20-m isobaths in 1994

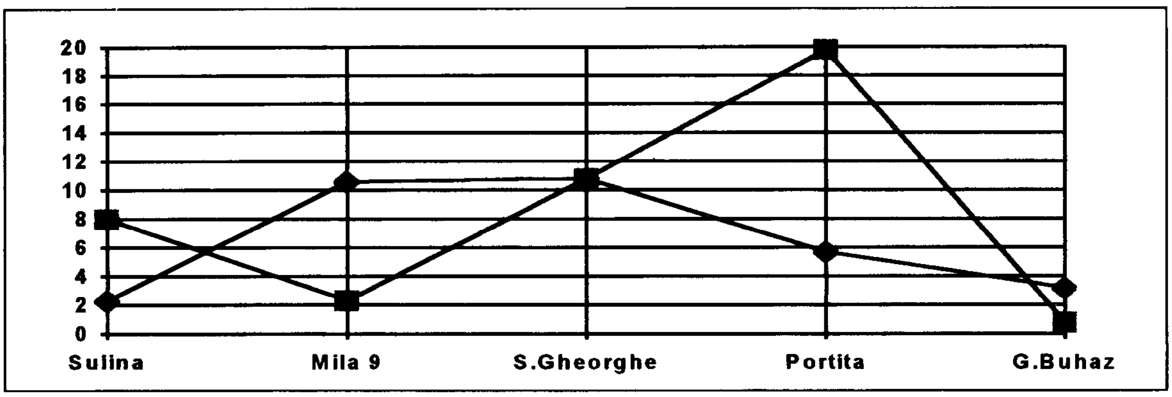

FIGURE 20. Spatial distribution of the average N-NO_2 (μM) contained in sediments from interstitial waters collected on 10 m and 20 m isobaths in 1994

CONCLUSIONS

Our recent studies incorporating the analyses of sediments and water samples off the Danube mouth area in 1996, indicate the presence of high contents of heavy metals (Cd, Cu and Pb), hydrocarbons, radionuclides and nutrients in the near-shore marine sediments. The degree of pollution of sediments is increased by the effect of hydrological factors which are specific of this area, as well as anthropogenic and terrigenous characteristics. The high level of pollution in sediments collected on the 20 m isobath is due to a combined effect of the decreasing sediment grain-size and a contributions from the Danube and other rivers discharging into the northwestern part of the Black Sea.

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PECULIARITIES IN THE DISTRIBUTION OF CHEMICAL ELEMENTS IN THE GEORGIAN SECTOR OF THE BLACK SEA

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ABSTRACT

In this paper, for the first time we have dealt in detail with chemical elements, their peculiarities in the distribution of marine sediments and their shape. It is demonstrated that the spectrum of chemical elements in bottom sediments of the region under study, almost completely depends on the river discharge into the sea; more specifically, on the processes occurring in the zone where sea and river waters are mixing.

INTRODUCTION

The main source of terrigenous material in the central and southeastern sectors of the Black Sea in Georgia, is represented by river alluvium. They are mainly distributed in the following provinces: the southern slope of the greater Caucasus (Khobi and Rioni rivers), the Anatolian highland (Chorokhi River) and the west end of the Adjara-Trialetian folded system of the Paleogene period (the rest of the rivers). Along the coastline (from the beach to the continental slope), dynamic systems may be distinguished. In the southern part of the region located in the boundaries of the Chorokhi River, these dynamic systems are located between the Chorokhi and Natanebi river mouths (Figure 1). In this system, the principal direction of beach-forming materials is south to north, but there are also low scale coastal directions, which have not any special influence on the dynamic processes of the region. It is noteworthy that at the end of the last century, after the construction of the Batumi seaport, the beach-forming material (>0,1 mm) could not move to the north of Batumi, although the coastline of the Bartskhana-Natanebi, including the shelf and the continental slope, are made up of relicts of the

Chorokhi river loads (approximately 15-20%). Between the Natanebi and Supsa rivers, terrigenous material migrated mainly to the north, although insignificant southward longshore current is also observed. The coastal zone between the Natanebi and Khobi rivermouths is the central section of the Poti dynamic system. Most of the year, its right angle is orientated towards the predominant westward waves; this is why in this place, longshore currents of permanent direction are not observed. Based on the regular distribution of terrigenous material in the coastal zone, areas of deposition and degradation are identified, and their day-to-day ecological conditions and the tendencies of their further development can be estimated. In the region, 60% of the beach go through degradation due to the scarcity of terrigenous material. In spite of the regularity of distribution of the terrigenous material, our aim is to define the mobilization, migration and deposition peculiarities of the marine sediments.

For this purpose, surface sediments were collected at specific depths (i.e., 3, 5, 7, 9,11,13 and 15 m) on 28 profiles perpendicular to the coast, at the southeastern inner shelf of the Black Sea, starting from the border between Georgia and Turkey (Figure 1). Samples were also collected from rivers (alluvial material) and from the seaports of Batumi and Poti. All the sediment samples obtained from the seabed are different in grain size, as well as mineralogy. These features determine the characteristics of distribution of the chemical elements contained in the sediments. Copper, Zn, Mn, Ni, Fe, and Pb were analyzed by atomic absorption spectrophotometry (AAS); Cr, V and Mo using the quantitative spectral analysis; Mn, Zn, Ni, Pb analyses by the AAS method was checked by the quantitative spectral analysis.

The distribution of sediments on the shelf and continental slope and their chemical composition are controlled by geochemical and physical processes taking place in the mixing area of sea and river waters. These processes include size- and density-sorting of particles on one hand, and hydrolysis, sorption, desorption, coagulation, precipitation processes, caused mainly by changes in water salinity and pH because of the water mixing, on the other hand. From the obtained results we can see that distribution of chemical elements is not a linear function of depth, but the relationship has a sinusoidal form.

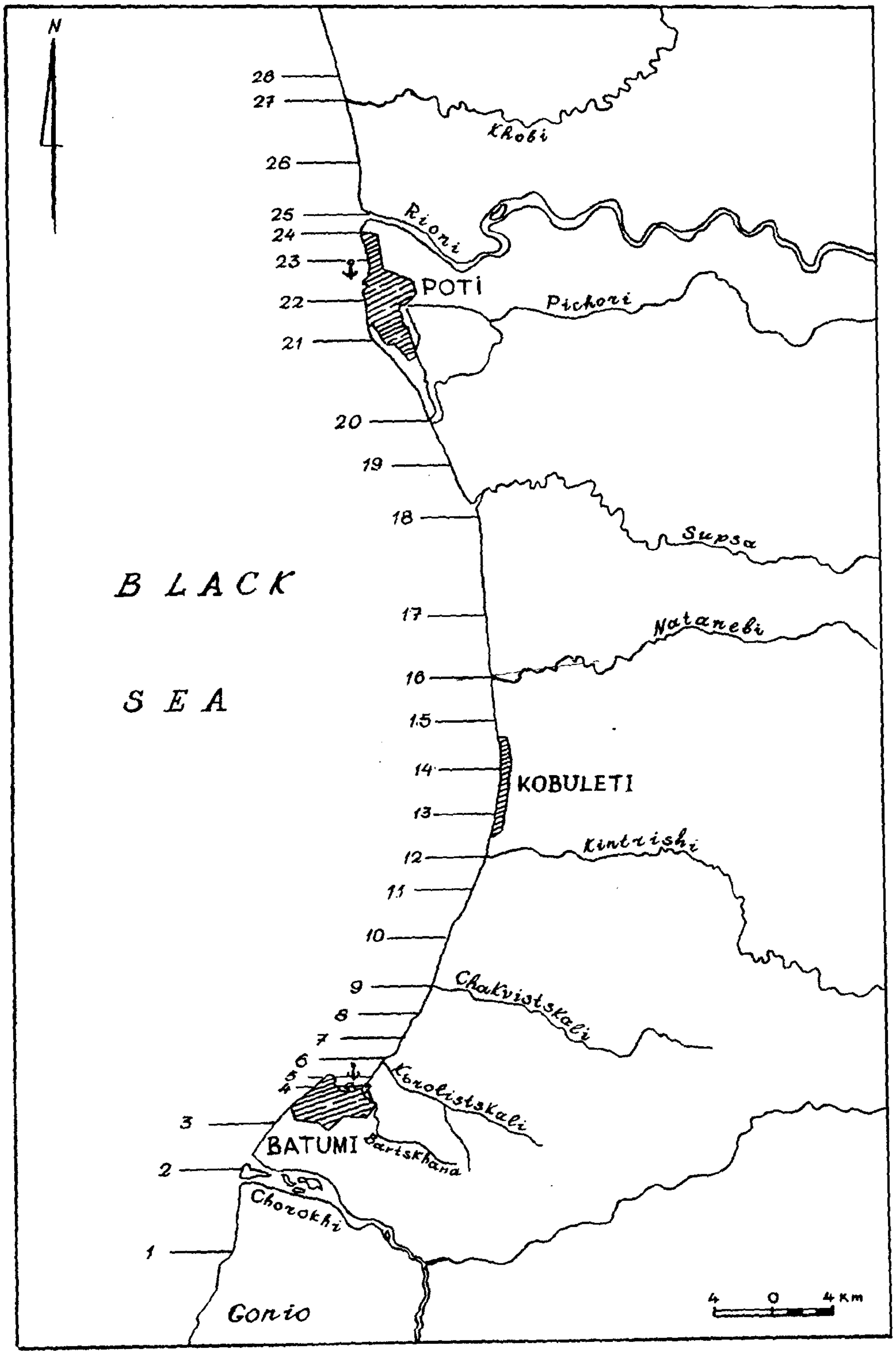

FIGURE 1. Distribution of Profiles.

DISTRIBUTION OF CHEMICAL ELEMENTS IN MARINE SEDIMENTS

Iron The Fe content in recently formed marine sediments varies within 4.8-12.2% (Table 1). The highest contents are observed on profile 4 at 9 m deep (12.2%), on profile 9 at 7 and 9 m deep (10.6-10.1%) and on profile 10 at 7 m deep (10.2%). On most profiles, the iron contents vary between 5.0 and 8.5%. The high Fe contents in these recent marine sediments are due to the presence of high amounts of magnetite, which are commonly concentrated at 7- 9 m deep by the hydrodynamic regime in the area.

Copper The maximum amount of Cu is observed on profile 2 at 3 m deep (0.13%) along the Chorokhi river mouth (Figure 1) . Southwards, on profile 1, there are no significant high Cu contents. To the north (profile 3) however, Cu concentrations increase to a range of 0.06-0.052% at 5 and 7 m deep. On profiles 4 to 7, high Cu contents (0.029-0.0057%) are observed at depths of 9, 11, 13 and 15 m. It is noteworthy that the Cu contents in the seaport of Batumi is also rather high, with a value of 0.055%. More at the north, on profiles 8-18, the Cu contents are low and almost evenly distributed in depth, with the exception of profile #10, where 0.035% of copper occurs at a depth of 7 m. In general, there is a decreasing tendency of Cu concentrations to the north of profile #15.

In profiles 2 and 3, the average Cu contents are the highest, with 0.29 and 0.31%, respectively . To the north, on profiles #5, #6 and #7, the average contents decrease until 0.022%, 0.020% and 0.029%, respectively. Still more at the north, the average Cu values abruptly decrease to almost the Clarke value of the element. The high concentrations of copper in sediments collected on profiles 2, 3, and 4 are mainly due to the presence of pyritic copper deposits, which are found in the Chorokhi catchment basin (Nazarov, 1966).

Zinc The maximum Zn content, as in the case of Cu, is found on profile 2 close to the Chorokhi river mouth. Other high Zn values are observed on profile 3, at 5 m (0.03%) and 7 m (0.027%) deep, and on profile 4 at 9 m (0.028%) and 15m (0.027%) down. On other profiles (1, and 5 to 28), high Zn concentrations are not observed. The average amount of Zn on profile 1 is equal to the Clarke value, but increases slightly on profiles 2 to 4 and 7. On profiles 5 to 17, it exceeds its Clarke value by about 1-1.5 times and in profiles 18-28 it decreases again to a generally lower value than the Clarke's one. As in the case of Cu, high Zn contents on profiles 2, 3, and 4 are the result of the presence of pyritic copper deposits in the Chorokhi catchment basin (Nazarov, 1966).

Vanadium. The V content ranges from 0.04 to 0.064 %. High V concentrations are observed on profiles 4 (7m deep), 9 (5 and 7 m deep), 13 (7m deep), 14 (13m deep), 15 (7 and 9 m deep) and 20 (15 m deep).

The average content of V in profiles 1 to 20 ranges between 0.013-0.029%. In profiles #21-28, the content considerably decreases, ranging between 0.006-0.009%, comparatively high amounts in profiles 1-20 are due to the presence of magnetite and biotite in the sediments.

Chromium High Cr concentrations are observed on profiles 4 (3,5,7 and 9 m deep), 6 (5 and 15 m deep), 9 (3 and 5 m of deep), 10 (5,7,11 and 15 m deep), 11 (11 and 15 m deep), 12 (5 and 7 m-deep), 13 (7 and 11 m deep), 14 (11 and 13 m deep) and #15 (7 m of depth). Its content ranges within 0.1-0.052%. In the other samples, Cr is considerably low and close to its Clarke value.

The average amount of Cr on profiles 1-3, 5, 7 and 19-28 is low. In all the other profiles, the comparatively high amounts result from the high contents of augite, biotite and magnetite in the sediments.

Manganese The distribution of Mn appears to be unrelated to water the depth. Considerably differing manganese contents are observed on the different profiles, but a generally significant increase in Mn content from south to north can be discerned.

The average content of Mn also shows an increase from south to north, reaching its highest values on profiles 20-23. This pattern suggests a rather high input of this element by the respective industrial and natural loads from the Rioni and Pichori rivers. The manganese content is also high in the industrially contaminated sediments of the seaport of Poti, but decreases to the north.

Molybdenum Among the rivers of the region, the Chorokhi is distinguished by high concentrations of molybdenum (4 10^{-4}%). This is shown in the maximum Mo content (4.1 10^{-4}%) on profile 2 (at 3 m deep) off the river mouth. The distribution of Mo does not show any relationship to depth.

The average content of molybdenum on profiles 1-15 ranges between 1.2-2.2 10^{-4}%. Northwards (profiles 16-18), it decreases to less than 1 10^{-4}%. The high content of molybdenum on profiles 1-15 depends on the high amount of pyrite in the solid drift of the Chorokhi River. It is estimated that from 16 to 100%, the molybdenum content in recent sediments is likely to be associated with pyrite (Mitropolskji et al., 1962).

Lead Pb shows an even distribution in depth on the various profiles, with the absence of any distinctly Pb-enriched area. Its concentration ranges within 0.007-0.0032%. The average content exceeds twice the background value. This high content is the result of the direct influence of the Poti seaport where the Pb content reaches its maximum (0.003%).

On profiles 1-3, the correlation coefficients between Fe-Cu and Fe-Zn are significantly at their maximum level (Table 2.). Northwards, the correlation coefficients between these elements decrease (Table 2.b-d). The strong and positive correlation between zinc and copper for all the profiles suggests a common source for these elements and their geochemical similarity. To the north of the studied region, the correlation coefficients between Fe-Cr and Fe-V reach a maximum. Here, the correlation between Fe-Cu is the lowest, although the significant and positive relationship between Fe-Zn observed in the south is preserved (Table 2).

From the above relationships, it can be assumed that on one hand, Fe takes part in the process of hydrolysis and co-precipitates with Cu and Zn and, on the other hand, together with V and Cr, it is delivered to the sea by rivers as detritus terrigenous material.

Cu, Zn and Pb concentrations in the recent marine sediments have been studied in different size fractions of three profiles (2-4) (Table 3). The results show that these elements are mainly concentrated in the 0.1-0.06 mm fractions.

TABLE 1. Concentration of Metals in sediments.

Profile number and water depth (m)	Concentration (%)						
	Fe	Cu	Zn	V	Cr	Mn	Mo (% 10^{-4})
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
# 1 3	6.9	0.011	0.013	0.021	0.008	0.11	1.5
5	5.7	0.009	0.009	0.023	0.004	0.09	1.6
7	6.6	0.01	0.011	0.031	0.003	0.1	1.7
9	4.8	0.01	0.009	0.014	0.009	0.08	2.7
11	5.7	0.014	0.01	0.01	0.002	0.07	2.0
13	5.4	0.014	0.008	0.012	0.002	0.07	1.7
15	4.5	0.022	0.009	0.011	0.002	0.07	2.4
R. Chorokhi	4.6	0.05	0.009	0.003	0.001	0.03	4.0
# 2 3	7.8	0.13	0.027	0.015	0.005	0.09	4.1
5	5.4	0.015	0.009	0.011	0.003	0.09	2.2
7	5.8	0.009	0.008	0.009	0.002	0.1	1.4
9	5.3	0.014	0.009	0.01	0.004	0.09	1.7
11	5.8	0.013	0.009	0.011	0.004	0.09	1.8
13	5.8	0.013	0.008	0.006	0.003	0.09	1.3
# 3 3	5.6	0.024	0.019	0.013	0.004	0.08	1.9
5	8.1	0.06	0.03	0.017	0.005	0.1	2.9
7	6.7	0.052	0.027	0.013	0.003	0.1	2.8
9	5.0	0.036	0.016	0.006	0.002	0.08	1.8
11	5.4	0.022	0.013	0.006	0.003	0.09	1.6
13	5.9	0.023	0.011	0.017	0.001	0.09	2.3
15	5.2	0.021	0.011	0.016	0.008	0.08	2.7
Port Batumi	3..9	0.055	0.014	0.017	0.006	0.04	3.7
R. Bartskhana	7.2	0.014	0.017	0.013	0.011	0.15	1.2
# 4 3	8.8	0.011	0.017	0.035	0.1	0.15	1.5
5	9.2	0.015	0.022	0.024	0.12	0.13	2.4
7	9.9	0.008	0.014	0.04	0.11	0.16	1.7
9	12.2	0.031	0.028	0.03	0.13	0.15	2.9
15	5.6	0.038	0.027	0.013	0.008	0.08	2.3
# 5 3	7.2	0.011	0.01	0.017	0.023	0.13	1.2
7	5.9	0.025	0.015	0.012	0.013	0.12	1.9
9	6.3	0.021	0.017	0.017	0.025	0.1	2.4
11	5.1	0.023	0.013	0.017	0.009	0.09	2.6
13	5.4	0.029	0.014	0.012	0.006	0.09	1.9
15	5.6	0.026	0.014	0.016	0.006	0.09	1.9
R.Korolistskali	3.8	0.01	0.037	0.006	0.014	0.1	1.1
# 6 3	6.9	0.008	0.013	0.024	0.023	0.12	1.3
5	8.7	0.008	0.016	0.037	0.086	0.15	1.4
7	6.0	0.01	0.012	0.025	0.026	0.12	1.5
9	6.3	0.013	0.012	0.024	0.016	0.12	1.6
11	6.8	0.057	0.021	0.021	0.026	0.11	2.5
13	6.0	0.015	0.015	0.019	0.025	0.12	2.5
15	5.5	0.016	0.012	0.014	0.01	0.11	1.9
# 7 11	5.0	0.018	0.015	0.014	0.009	0.11	2.1
13	8.0	0.036	0.022	0.02	0.034	0.13	3.1
15	5.7	0.032	0.017	0.008	0.003	0.11	2.2
# 8 9	9.6	0.007	0.015	0.035	0.056	0.17	2.2
11	7.7	0.006	0.012	0.03	0.058	0.14	1.8
13	5.7	0.006	0.01	0.013	0.011	0.12	1.4
15	5.7	0.006	0.009	0.012	0.008	0.12	1.4
R.Chakvictskali	8.0	0.013	0.009	0.005	0.003	0.16	1.1
# 9 3	8.1	0.013	0.012	0.031	0.056	0.13	1.3
5	7.5	0.011	0.011	0.045	0.064	0.13	1.1

Profile number and water depth (m)		Concentration (%)					
	Fe	Cu	Zn	V	Cr	Mn	Mo (% 10^{-4})
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
7	10.6	0.006	0.014	0.047	0.11	0.18	1.5
9	7.4	0.008	0.013	0.025	0.04	0.14	1.1
11	7.1	0.012	0.011	0.019	0.019	0.12	1.4
13	10.1	0.011	0.016	0.038	0.048	0.16	1.4
15	7.9	0.008	0.014	0.038	0.048	0.15	1.5
# 10 3	5.6	0.011	0.011	0.012	0.016	0.11	< 1
5	7.8	0.009	0.015	0.03	0.068	0.15	1.3
7	10.2	0.035	0.03	0.026	0.062	0.15	4.0
9	6.3	0.006	0.012	0.014	0.024	0.13	1.2
11	7.7	0.006	0.013	0.03	0.054	0.15	1.5
15	8.8	0.006	0.015	0.02	0.054	0.16	1.9
# 11 5	6.2	0.01	0.012	0.012	0.009	0.27	1.8
7	9.7	0.008	0.017	0.024	0.04	0.22	2.0
9	6.1	0.006	0.011	0.011	0.013	0.15	1.3
11	8.1	0.005	0.015	0.028	0.056	0.16	1.9
15	9.3	0.005	0.015	0.026	0.058	0.17	2.6
R. Kintrishi	10.2	0.012	0.012	0.011	0.023	0.17	< 1
# 12 5	7.2	0.009	0.014	0.025	0.058	0.25	1.6
7	7.7	0.008	0.014	0.028	0.054	0.26	1.7
9	7.5	0.006	0.013	0.017	0.044	0.2	1.5
# 13 7	10.2	0.026	0.025	0.042	0.078	0.2	1.5
9	7.2	0.012	0.014	0.028	0.041	0.21	1.1
11	7.9	0.012	0.015	0.028	0.052	0.22	1.1
13	6.7	0.014	0.012	0.021	0.04	0.17	-
15	6.4	0.016	0.011	0.014	0.024	0.12	0
# 14 11	8.1	0.013	0.014	0.028	0.072	0.16	1.2
13	8.3	0.007	0.013	0.04	0.088	0.17	1.4
15	6.1	0.012	0.012	0.018	0.036	0.17	1.1
# 15 3	6.8	0.007	0.011	0.026	0.048	0.13	1.0
5	5.6	0.007	0.016	0.026	0.036	0.12	1.0
7	7.0	0.006	0.014	0.04	0.074	0.16	1.1
9	7.7	0.008	0.012	0.045	0.11	0.16	1.2
11	6.4	0.008	0.011	0.019	0.041	0.15	0
13	6.3	0.011	0.012	0.018	0.025	0.15	0
15	6.0	0.009	0.011	0.028	0.042	0.14	1.0
R. Natanebi	5.5	0.01	0.01	0.014	0.044	0.13	1.1
# 16 3	5.4	0.005	0.01	0.024	0.039	0.14	1.1
5	6.3	0.005	0.011	0.028	0.048	0.15	1.1
7	9.8	0.007	0.015	0.035	0.1	0.18	1.3
9	7.2	0.008	0.013	0.028	0.1	0.18	1.0
11	6.1	0.009	0.011	0.013	0.04	0.16	0
13	5.8	0.011	0.011	0.025	0.018	0.11	1
15	5.6	0.012	0.011	0.014	0.012	0.11	1
# 17 3	7.1	0.007	0.014	0.031	0.023	0.18	1
5	7.7	0.006	0.015	0.025	0.06	0.28	1
9	6.1	0.007	0.014	0.018	0.029	0.24	< 1
11	5.9	0.006	0.012	0.021	0.029	0.22	< 1
13	5.8	0.008	0.011	0.009	0.016	0.20	< 1
15	5.5	0.008	0.012	0.01	0.012	0.19	< 1
# 18 3	9.8	0.006	0.014	0.052	0.1	0.29	< 1
5	5.0	0.005	0.009	0.015	0.013	0.38	< 1
7	5.6	0.006	0.009	0.012	0.012	0.3	< 1
9	4.9	0.007	0.009	0.017	0.022	0.34	< 1

Profile number and water depth (m)	Concentration (%)						
	Fe	Cu	Zn	V	Cr	Mn	Mo (% 10^{-4})
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
11	4.8	0.008	0.009	0.015	0.013	0.21	<1
13	5.4	0.011	0.009	0.017	0.015	0.15	<1
15	5.2	-011	0.09	0.014	0.012	0.21	<1
R. Supsa	7.0	0.009	0.009	0.018	0.1	0.13	< 1

Profile number and water depth (m)		Concentration (%)					
		Zn	V	Cr	Mn	Ni	Pb
# 19	9	0.004	0.004	0.006	0.26	0.004	0.0020
	11	0.008	0.006	0.006	0.11	0.006	0.0023
	13	0.007	0.016	0.006	0.22	0.005	0.0025
# 20	3	0.008	0.017	0.005	> 0.4	0.005	0.0025
	5	0.008	0.011	0.003	> 0.4	0.004	0.0020
	7	0.006	0.017	0.007	> 0.4	0.005	0.0021
	9	0.007	0.014	0.004	0.31	0.006	0.0020
	11	0.008	0.016	0.005	> 0.4	0.005	0.0015
	15	0.011	0.064	0.006	0.33	0.003	0.0020
R.Pichori		0.007	0.011	0.006	< 0.4	0.003	0.0007
# 21	3	0.011	0.008	0.011	>0.4	0.003	0.0015
	5	0.01	0.006	0.006	> 0.4	0.003	0.0021
	7	0.011	0.008	0.01	> 0.4	0.003	0.0010
	9	0.012	0.006	0.005	> 0.4	0.005	0.0025
	11	0.01	0.007	0.007	> 0.4	0.003	0.0031
	13	0.009	0.009	0.007	> 0.4	0.003	0.0025
	15	0.01	0.006	0.007	> 0.4	0.002	0.0020
# 22	3	0.01	0.005	0.005	> 0.4	0.002	0.0023
	5	0.013	0.005	0.006	0.27	0.003	0.0023
	7	0.011	0.009	0.007	0.31	0.004	0.0032
	9	0.014	0.008	0.006	> 0.4	0.005	0.0023
	11	0.009	0.01	0.007	0.12	0.003	0.0025
	13	0.008	0.007	0.006	0.06	0.003	0.0021
	15	0.009	0.007	0.007	0.12	0.003	0.0016
# 23	3	0.011	0.004	0.003	> 0.4	0.005	0.0015
	5	0.009	0.003	0.003	0.07	0.005	0.0007
	7	0.009	0.006	0.007	0.26	0.003	0.0028
	9	0.009	0.006	0.007	0.31	0.003	0.0018
	11	0.008	0.01	0.007	> 0.4	0.002	0.0011
	13	0.009	0.008	0.006	> 0.4	0.003	0.0028
	15	0.011	0.008	0.006	> 0.4	0.004	0.0025
Port Poti		0.007	0.005	0.015	> 0.4	0.005	0.003
# 24	3	0.013	0.011	0.01	> 0.4	0.004	0.0018
# 25	3	0.009	0.007	0.005	0.23	0.004	0.0021
	9	0.006	0.01	0.05	0.08	0.003	0.0021
# 26	3	0.008	0.012	0.07	0.08	0.005	0.0023
	5	0.006	0.007	0.06	0.21	0.002	0.0018
# 27	7	0.008	0.01	0.1	0.23	0.004	0.0013
	9	0.006	0.009	0.06	0.18	0.003	0.0015
# 28	3	0.007	0.005	0.06	0.04	0.004	0.0021
	5	0.007	0.01	0.05	0.07	0.004	0.0016
	7	0.009	0.006	0.08	0.23	0.003	0.0016
	9	0.006	0.008	0.05	0.31	0.002	0.0016

TABLE 2. Correlation coefficients.

a. Profil N 1 -3						b. Profile N 4 – 8					
	Mn	Cr	V	Zn	Cu		Mn	Cr	V	Zn	Cu
Fe	0.65	-0.14	0.12	0.75	0.64	Fe	0.82	0.92	0.8	0.59.	-0.15
Cu	0.12	0.09	-0.14	0.79	-	Cu	-0.46	-0.26	-0.9	0.53	-
Zn	0.4	0.16	-0.12	-	-	Zn	0.17	0.55	0.22	-	-
V	0.4	-0.16	-	-	-	V	0.81	0.81	-	-	-
Cr	-0.06	-	-	-	-	Cr	0.74	-	-	-	-
Mn	-	-	-	-	-						

c. Profile N 9 –12						d. Profile N 13 – 18					
	Mn	Cr	V	Zn	Cu		Mn	Cr	V	Zn	Cu
Fe	0.07	0.72	0.71	0.64	0.23	Fe	-0.5	0.82	0.82	0.68	0.31
Cu	-0.14	0.05	-0.02	-	-	Cu	-0.44	0	0.03	0.36	-
Zn	0.07	0.32	0.31			Zn	-0.51	0.49	0.54	-	-
V	0.12	0.68	-	-	-	V	-0.47	0.85	-	-	-
Cr	0.04	-	-	-	-	Cr	-0.4	-	-	-	-

TABLE 3. Metal contents in 0,1-0,06 mm fractions.

PROFILE #	DEPTH (M)	%		
		Cu	Zn	Pb
2	3	0,400	0.100	0.016
	5	0.170	0.051	0.006
3	3	0.130	0.060	0.008
	5	0.090	0.040	0.006
	7	0.052	0.025	0.004
	9	0.029	0.017	0.002
	11	0.019	0.015	0.002
4	3	0.011	0.023	0.0055
	5	0.014	0.019	0.003
	7	0.009	0.025	0.0020
	9	0.062	0.040	0.0045

MODE OF OCCURRENCE OF THE ELEMENTS IN THE SEDIMENTS

To identify the chemical forms of elements in sediments, samples have been selected in different settings. For example, the Pechori River constitutes a natural swampy ecosystem where anthropogenic inputs are negligible, whereas the rest of samples were selected in areas under considerable anthropogenic influence (Table 4).

In order to define the chemical forms of the elements, successive selective extractions – also including the Chester's reagent and followed by AAS analyses - were used.

Iron The Fe content in fluvial and marine sediments vary between 3,08 and 4,54%. The main part of this iron occurs during the lithogenic phase, with contents exceeding 70% of the total iron content in the oxide phase (Table 4). The sediments of the Batumi seaport are an exception, where the ratio Fe in the oxide phase constitutes only 56,2% and in the hydroxide phase 6,6-8,86% of total iron contents.

The fraction of labile Fe is very low and ranges from 1.43% in the Chorokhi sediments up to 9.53% in the Batumi port sediments. Northwards, this slight shift to more soluble forms is probably caused by hydrolysis of sulphide minerals present in the Chorokhi river deposits. As already mentioned, sources of these minerals occur in the catchment basin of the river.

Manganese The total contents of Mn in the Rioni and Pichori Rivers and in the Poti seaport sediments are 0.203%, 0.231% and 0.28%, respectively (Table 4). In these sediments, the major fraction of Mn occurs in the labile form, constituting 46.38%, 71.44%, 80.3% of the total contents. In the marine sediments, influenced by these Rioni and Pichori Rivers, the contents of Mn in the labile phase is also high.

In the sediments of the Chorokhi and Batumi Rivers, the concentration of during the lithogenic phase is high, ranging from 35.3% to 38.8%, but the Mn fraction in the labile phase is reduced to 28.3% - 40.7%. As in the case of Fe, the lithogenic Mn phases are changing into more soluble forms in the sediments of the Batumi seaport, probably due to the hydrolysis of minerals.

Zinc As in the case of Fe, Zn occurs mainly under the lithogene oxide form, constituting >40% of the total Zn content (Table 4). The rest of Zn is distributed between the hydroxide, silicate and labile phases. In the sediments from the Chorokhi River and Batumi seaport, the element contents occurring in the labile form have increased up to 36.1% and 51% of the total Zn (299 and 488 ppm), respectively.

Copper Cu is characterized by its considerably low content of labile form compared to Zn. Its content is more evenly distributed between lithogenic fractions than in the case of Zn, although the prevalence of the oxide form is still preserved.

As in the case of Fe and Zn, in the Batumi seaport marine Cu sediments under labile form constitute up to 25%, and the organic fraction up to 29% of the total Cu.

Unlike other elements, a definite fraction of Cu (from 21.7% to 52.5%) is a component of silicate minerals. Locally, in the sediments of the Pichori river and Poti seaport as well as northwards in marine sediments, the Cu content in the silicate and residual fractions is negligible.

CONCLUSIONS

Regularities in the distribution of metals in marine and alluvial sediments from the Georgian sector of the inner Black Sea shell have been investigated and the degree of dependence of this distribution on water depth and grain-size of sediments was established.

Two types of marine sedimentation have been identified on the sea-floor: (a) sedimentation of the material mechanically transported (i.e., lithodynamic type), and (b) deposition of amorphous phases formed as a result of hydrolysis (i.e., hydrochemical sedimentation). Two areas of high metal accumulation have been identified where the metals are predominantly of industrial origin; these areas are associated with the inputs from the Chorokhi and Rioni rivers. The sediments in the vicinity of the Batumi and Poti seaports are also characterized by high metals contents.

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TABLE 4. Content of metal forms in sediments

		Fe, %							Mn, %						
		Σ	I	II	III	IV	V	VI	Σ	I	II	III	IV	V	VI
1	r. Rioni	3.6	0.10	0.016	0.26	2.69	0.5	0.035	0.203	0.094	0.066	0.016	0.023	0.02	0.02
			2.8	0.45	7.2	74.7	13.8	0.97		46.38	32.55	7..9	11.3	9.8	9.8
2	r.Chorokhi	4.54	0.065	0.04	0.27	3.34	0.8	0.022	0.06	0.017	0.004	0.003	0.032	0.002	0.002
			1.43	0.88	5.95	73.6	17.6	0.48		28.3	6.7	5.0	53.3	3.3	3.3
3	r.Pich-ori	3.78	0.3	0.08	0.25	2.72	0.4	0.034	0.231	0.165	0.027	0.009	0.025	0.002	0.003
			7.9	2.1	6.6	72	10.6	0.9		71.4	11.7	3.9	10.8	0.7	1.3
4	Poti port	3.8	0.27	0.03	0.3	2.68	0.52	0.014	0.28	0.225	0.018	0.01	0.024	0002	0.001
			7.1	0.79	7.87	70.3	16.8	3.79		80.3	6.4	3.6	8.6	0.7	0.4
5	Batumi port	3.86	0.36	0.2	0.62	2.17	0.5	0.009	0.054	0.022	0.007	0.003	0.021	0.001	0.0
			9.3	5.2	16.1	56.2	12.9	0.22		40.7	12.2	5.6	38.8	1.9	0.0
6	pr. N20	3.08	0.11	0.018	0.23	2.35	0.3	0.03	0.477	0.33	0.105	0.02	0.02	0.001	0.0
			3.6	0.58	7.47	76.3	11.0	0.97		69.2	22.0	4..2	4.2	2.1	0.0
7	pr. N21	3.17	0.1	0.021	0.22	2.51	0.3	0.016	0.38	0.25	0.084	0.022	0.023	0.001	0.001
			3.15	0.66	6.94	79.18	9.46	0.5		65.8	22.0	5.8	6.1	2.6	2.6
8	pr. N22	3.95	0.16	0.044	0.35	3.07	0.3	0.029	0.196	0.15	0.015	0.008	0.02	0.001	0.001
			4.05	1.1	8.86	77.7	7.7	0.73		76.5	7.6	4.1	10.2	5.1	5.1

TABLE 4. (cont.)

		Zn. Ppm							Cu. ppm						
		Σ	I	II	III	IV	V	VI	Σ	I	II	III	IV	V	VI
1	r. Rioni	158	12 7.6	18 11.4	25 15.8	70 44.3	30 19	3 1.9	281	12 4.3	6 2.1	50 17.8	50 17.8	144 51.2	19.2 6.8
2	r.Chorokhi	299	108 36.1	33 11	35 11.7	90 30.1	30 10.0	3 1.0	328	27 8.2	93 28.3	60 18.3	70 21.3	78 23.8	5.4 1.6
3	r.Pichori	166	24 14.4	18 10.8	30 18.1	80 48.2	10 6.0	4 2.4	119	27 22.6	12 10.2	30 25.2	50 42	0.0 0.0	0.0 0.0
4	Poti port	185	36 19.5	18 9.7	30 16.2	80 43.2	20 10.8	0.0 0.0	95	21 22.1	9 9..5	25 26.3	40 42	0.0 0.0	0.0 0.0
5	Batumi port	488	249 51.0	84 17.2	45 9.2	80 16.4	30 6.1	10 2	553	138 25	162 29.3	65 11.8	60 10.8	120 21.7	8.5 1.5
6	pr. N20	141	51 10.6	21 14.9	25 17.7	70 49.6	10 7.1	0.0 0.0	72	9 12.5	3 4.2	30 41.7	30 41.7	0.0 0.0	0.0 0.0
7	pr. N21	158	18 11.4	27 17.1	30 19.0	70 44.36	10 6.3	3 1.9	140	9 6.4	6 4.3	40 28.6	40 28.6	45 32	0.0 0.0
8	pr. N22	181	18 9.9	15 8.3	35 19.3	90 49.7	20 11.0	3 1.7	219	12 5.5	9 4.1	25 11.4	50 22.8	115 52.5	7.5 3.4

Numerator - concentration in mg/kg. denominator percentage of the total extracted metal.

I. Easily soluble fraction (1 N acetic acid); II. Organic fraction (30% H_2O_2); III. Mn- and Fe-oxyhydroxide fraction (Chester Reagent); IV. Crystalline oxide fraction (HNO_3 + HCl); V. Lithogenic fraction 1 (HF + HCl); VI. Lithogenic fraction 2 ($HClO_4$ + HCl + HNO_3).

RIVERINE INPUT OF POLLUTANTS FROM GEORGIA IN THE BLACK SEA BASIN

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ABSTRACT

The rivers Rioni, Enguri and Chorokhi supply the highest fresh water flow among the rivers entering the Black Sea from the Georgian territory. The data collection on pollutants from the lower course of these rivers started in 1986, as part of a national programme. The analysis of these data shows that the more important pollutants are phenol, oil and nitrogen nitrates.

INTRODUCTION

The ecological situation in the Black Sea has turned worse during the last few decades. The increasing anthropogenic activity has caused raises in the concentration of pollutants which, in turn, added to the ecologic problems of the Black Sea. One of the main sources of pollution in the Black Sea is the flow of dissolved polluted substances via large rivers.

There are about 150 rivers of various sizes in Georgia, flowing into the Black Sea. The chemical composition of the river water is determined by a complex interaction of natural (e.g., rock weathering) and anthropogenic (e.g., input of municipal, industrial and agricultural contaminants) processes in the drainage basin.

The major source of fresh water, as well as polluting components delivered to the Black Sea from Georgia are proceeding from the Rioni, Enguri and Chorkhi rivers. These rivers differ from others by their large drainage areas which represent nearly half of the Western Georgian territory. Major industrial and economic activities of Georgia are concentrated in the drainage basins of these rivers. It is estimated that about 60% of the pollution introduced to the Black Sea from Georgia is via these three rivers,and 31% from the only Rioni river (Chantladze, 1985). Waste water discharges constitute the main source of pollution in the Rioni river and its many tributaries, the largest of which are the Tskhenistskali and the Kvirila. Various large industrial plant are located in the drainage basins of this river and its tributaries. These include the Chiatura manganese mining industry, Zestafoni ferroalloy plant, and Kutaisi automobile industry. The main polluting elements for the Enguri river are the ceramic and paper factories in Zugdidi.

The "Water Hygiene and Safety" Group at the S/R Institute of Sanitation and Hygiene of the Georgian Ministry of Health has been carrying out a research programme on Water Safety and Treatment since 1926. Since 1994, the Group has been involved in the BSEP (Black Sea Environmental Programme). This paper presents some data on the average concentration of pollutants discharged into the Black Sea via the rivers Rioni, Enguri and Chorokhi, during the period 1986-1995. The pollutants measured in the water include nutrients, oil, phenols, detergents and some heavy metals. The sampling was conducted in large cities (Zestaphoni, Chiatura Samtredia, Abasha, Kutaisi, port Poti, Zugdidi, Anaklia and Batumi), in the area upstream and downstream from the pollution sources (as a model), as well as at the river mouth. These sampling locations include Zestaphoni and Chiatura on the Kvirila River; Samtredia on the Tskhenistskali River; Abasha, Kutaisi and port Poti on the Rioni River; Zugdidi and Anaklia on the Enguri River; and Batumi on the Chorokhi River. The various contents of pollutant in the water samples have been analyzed using standard analytical methods. Heavy metals were analyzed by atomic absorption spectrophotometry (AAS), mineral oil by gravimetry, phenol by the 4-amino-anty-pirin method; ammonium by the Nesler's method, nitrate by a spectrophotometric method using DSPh acid, the biochemical oxygen demand (BOD) by the standard BOD test using the BOD bottles, and the dissolved oxygen (DO) by the Winkler's method. The monthly amounts of pollutants delivered to the sea were computed by multiplying the average flow in the river water. The annual discharge of each pollutant was obtained by adding the monthly amounts.

RESULTS

Heavy Metals

Heavy metals in the river water are originated either by natural processes or human activities. Leaching of mine tailings and drainage from mine areas can introduce substantial amounts of metals into the river (Olade, 1992). The total amount of dissolved metal delivered to the Black Sea by the Geogian rivers equals $10.5.10^6$ t/yr. Among the heavy metals, discharges of Cu, Ni and Mn to the Black Sea are significant. The dissolved amounts of these metals delivered to the Sea by the three largest Georgian rivers (i.e., Rioni, Enguri, and Chorokhi) are estimated by monitoring the metal concentrations and the water flow at the mouth of these rivers. According to the monitoring programme, the dissolved amounts delivered by the Enguri River are 15.4 t Ni/yr, 18.24 t Mn/yr and 33.2 t Cu/yr; by the Rioni River 29.6 t Ni/yr, 104.2 t Mn/yr and 144.2 t Cu/yr; and by the Chorokhi River 12.4 t Ni/yr, 25.2 t Mn /yr, and 22.1 t Cu-/year (Table 1; Figure.1). The amount of Cu and Ni constitutes 34-48% of the total discharge of heavy metals. The annual average of metal concentrations in waters of the Enguri River are 2 ppb Cu, 6 ppb Zn, 0.5 ppb V, 0.4 Mo and 51 ppb Fe, and in the Rioni River 6 ppb Cu, 21 ppb Zn, 4 ppb V, 20 ppb Mn and 89.6 ppb Fe.

TABLE 1. The amount of heavy metals (t/yr) delivered to the Black sea by river waters. Measurements were made at the river mouths.

River	Fe	Pb	Mn	Ni	Cu
Rioni	293.6	4.05	104.2	29.6	144.2
Enguri	229.8	18.1	18.2	15.4	33.2
Chorokhi	200.6	27.3	25.2	12.4	22.05

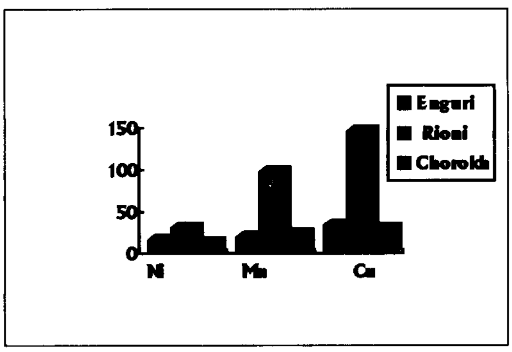

FIGURE 1. Input of dissolved heavy metals (t/yr) to the Black Sea via the large Georgian rivers.

Nutrients, DO and BOD

Nutrients are chemical elements and compounds in the environment from which living organisms synthesize living matter, including their body cells, tissues, genetic material, energy bearing molecules and reproductive cells. In this study, nitrate, nitrite and ammonium were determined. Nitrates and nitrites in high concentrations are known to have toxic effects on the environment. Ammonium is also known to be toxic for aquatic organisms.

The sources of nutrients in river waters can be broadly divided into natural and anthropogenic sources. Natural sources are generally omnipresent. Anthropogenic sources result from many activities, including the use of fertilizers as well as discharge of domestic (municipal) and animal dejections. The average ammonium and nitrate-N concentrations in the large Georgian rivers, together with their annual amounts supplied to the Black Sea via the river waters, are presented in Table 2.

TABLE 2. Concentration and annual amounts of ammonium and nitrate-N delivered to the Black Sea by Rioni, Engori and Chorokh river waters

River	Ammonium		Nitrate	
	mg/l	t/yr	mg/l	t/yr
Rioni	0.2-0.3	1303	0.7-1.0	8161
Enguri	1.0-2.0	1101	1.7	1887
Chorokhi	0.25	427.2	0.8	6933

The most important indicators of water pollution are BOD and DO, which depend on the organic matter content, and in particular on the amount of the non-stable organic substances. The DO and BOD of the Rioni River water downstream from Poti are 1,9 mg/l and 2,28mg/l, respectively. In the Enguri River, the DO is 7,1mg/l and BOD 1,36mg/l. These values demonstrate, to some extent, the influence of the discharges originated by the paper industry on the quality of the Enguri River water. However, the Enguri is a very fast, full flowing river that reaches very rapidly the full DO saturation level at the river mouth (Lashkhauri and Zalkaliani,1986).

Surface Active Substances, Oils and Phenols

The synthetic organic chemical composition of municipal wastewater is the result of various products supplied by industrial effluents. The daily determination of SAS (Surface-Active Substances or methylene-blue-active substancies) in the river waters, shows that in the samples collected downstream from Kutaisi, the SAS content is 0.27mg/l, but decreases by dilution to 0.03mg/l downstream from Poti.

Other hazardous substances are oil and phenols discharged into the rivers. The pollution by these substances causes irrecoverable damages to marine flora and fauna. The study of oil and phenols contents in water, sampled in all the places previously mentioned, help us to determine their oil concentration in the Enguri River is 0.5 mg/l, and the amount of oil discharged by this river is 63.3 t/yr. The average oil concentration in the Rioni River and its annual amount delivered to the Black Sea are relatively high, reaching respectively 0.84 mg/l and 652 t/yr.

CONCLUSIONS

The results of this study show that the major pollutants transported by the main Georgian rivers to the Black Sea are ammonium-N, phenols, oil, Cu and Zn. The maximum concentration of oil in the sea water sampled close to the river mouths increases up to 2 to 25 times the average concentrations. On the basis of time-series observations of oil and phenol concentrations in the sea water and river water, we consider that the main pollution of sea waters by oil and phenols is not induced by the river fluxes, but by industrial discharges from the coastal zone. The Batumi oil treatment plant, Batumi oil storage, Batumi and Poti ports are regarded as the main polluting sources.

The Black Sea and its coastal zone are strategically important for the economic development of Georgia. However, an industrial development programme without proper environmental protection measures could cause a serious ecological damage to the Black Sea.

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RECONSTRUCTED INTERANNUAL FLUXES OF DISSOLVED Cs^{137}, Cs^{134} AND Sr^{90} PUMPED INTO THE BLACK SEA BY THE DANUBE AND DNIEPER RIVERS FROM 1986 TO 1994

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ABSTRACT

The problem of radionuclide pollution of the Black Sea by the isotopes Cs^{137}, Cs^{134} and Sr^{90} has been discussed. Radionuclide fluxes of dissolved cesium and strontium by the Danube and Dnieper in 1986 to 1994 have been reconstructed. There has been an estimation of the amount of radionuclides in sediments. It is demonstrated that there is at present a specific process of self-refining of the Black Sea water from radionuclides. The principle sources and drains of dissolved Cs^{137} in the Black Sea have been identified and their contribution to the pollution of the Black Sea by radionuclide has been calculated. In conclusion, the dissolved radionuclide fluxes delivered by the Danube and the Dnieper Rivers to the Black Sea contribute to its radionuclide pollution, but in a negligible way compared to another contributor of pollution: the atmosphere.

INTRODUCTION

The investigations on the dispersion of the radioactive mushroom cloud from Chernobyl, which occurred during the last 11 years, revealed a considerable spatial heterogeneity. These studies include some rough estimates of the radioactive levels realized by *Izrael et al.* [1992]. The present objective is to study the predictability of radioactive pollution in various geographic regions affected by the Chernobyl accident. To this end, estimations of the initial distribution must be specified, as well as the quantitative description of the temporal evolution of radionuclides, and the identification of different sources and sinks of these pollutants.

The Danube and Dnieper rivers constitute potential sources of radionuclide pollution of the Black Sea, which might carry a large amount of nuclides after the Chernobyl accident. Unfortunately, there are no records of regular measurements of such radionuclide fluxes for 1986-1994. Therefore, there are no actual estimations of the radionuclide fluxes regarding these rivers during the period mentioned. The present study has reconstructed the fluxes of Cs^{137}, Cs^{134} and Sr^{90} delivered by the Danube and Dnieper rivers into the Black Sea on the basis of the data collected by the former USSR scientists from 1986 to 1994.

DATABASE

The data utilized in our analysis were obtained from scientific studies carried out onboard R/Vs *Yakov Gakkel*, *Professor Kolesnikov*, *Professor Vodyanitsky*, *Trepang* and *Akademik Vernadsky*, archived in the database of the Marine Hydrophysical Institute. The temporal structure of the data series is indicated in Table 1. The data collected in 1986 and 1992 had been previously used by Eremeev et al. (1994, 1995) to estimate the amount of dissolved Cs^{137} and Cs^{134} in the Black Sea.

TABLE 1. Post-Chernobyl Black Sea radioactive pollution in the Black Sea from 1986 to 1994.

Month, year	Isotope	number of stations	station type	R / Vs
June, July 1986	Cs^{137}, Cs^{134}	18	surface	33 *v.Akademik Vernadsky*
October, 1986	Cs^{137}, *Tr*, Sr^{90}	24	deep	27 *v. Yakov Gakkel*
November, 1986	Cs^{137}, Cs^{134}	23	surface	14 *v. Professor Kolesnikov*
December, 1986	Cs^{137}, Cs^{134} Cs^{137}, Cs^{134}	50 1	surface deep	14 *v. Professor Kolesnikov*
May, 1987	Cs^{137}, Cs^{134}	12	surface	23 *v. Professor Vodyanitsky*
June, 1987	Cs^{137}, Cs^{134}	52	surface	23 *v. Professor Vodyanitsky*
July, August 1987	Cs^{137}, Cs^{134} Cs^{137}, Cs^{134}	6 13	deep surface	36 *v. Akademik Vernadsky*
September, 1987	Cs^{137}, Cs^{134}	30	surface	*Supsa*
April, May 1988	Cs^{137}, Cs^{134} Cs^{137}, Cs^{134}	37 2	surface deep	37 *v. Akademik Vernadsky* 18 *v. Professor Kolesnikov*
June, July 1988	Cs^{137}, Cs^{134}	18	surface	18 *v. Professor Kolesnikov*
October, 1988	Cs^{137}, Cs^{134}	10	surface	37 *v. Akademik Vernadsky*
April, 1989	Cs^{137} Cs^{134}	39 23	surface surface	21 *v. Professor Kolesnikov*
June, 1989	Cs^{137} Cs^{134}	17 4 16 4	surface deep surface deep	22 *v. Professor Kolesnikov*
July, 1989	Cs^{137} Cs^{134}	20 3 18 2	surface deep surface deep	22 *v. Professor Kolesnikov*
August, 1991	Cs^{137}, Sr^{90} Sr^{90} *Pu*	26 23 5	surface sediment sediment	*Trepang*
July, August, 1992	Cs^{137}	18	deep	21 *v. Professor Kolesnikov* 40–A *v. Yakov Gakkel*
April, 1993	Cs^{137}, Sr^{90}	60	surface	30 *v. Professor Kolesnikov*
August, 1993	Cs^{137}, K^{40}, Th^{232}	9	sediment	
December, 1994	Cs^{137}	43	surface	32 *v. Professor Kolesnikov*

RECONSTRUCTION PROCEDURE

The special reconstruction procedure developed by Ivanov and Margolina (1996), Eremeev et al. (1994, 1995,1997) and Danilov et al. (1996) has been used in the present study, for the estimation of fluxes pumped into the Black Sea by the Danube and Dnieper rivers.

Let us briefly discuss the mathematical approach to the reconstruction of radionuclide fluxes through an arbitrary liquid boundary of the sea, on the basis of the data collected within the marine basin. According to the reconstruction procedure, the concentration of the *i*th radionuclide at an arbitrary point *p* of the sea with the coordinates $\overset{]\,o}{w}+y^{o}$ may be represented as the special series

$$c_i\left(\hat{x}_\perp^{p}, z^{p}, t\right) = \sum_{n=1}^{N} A_n^i\left(t, z^{p}\right)\Psi_n\left(\vec{x}_\perp^{p}, z^{p}\right) \qquad (1)$$

where $\vec{w}_{\perp}+y$ are the horizontal and vertical spacings, respectively; $A^i{}_n$ are the spectral coefficients, Ψ_n are the basic functions which should be determined as the solution of the following spectral problem:

$$\Delta\Psi_m = -\lambda_m\Psi_m \tag{2}$$

$$\left.\frac{\partial\Psi_m}{\partial\lambda}\right|_{\Gamma} = / \tag{3}$$

where Δ and λ_n are the plane Laplace operator and its Eigen values, respectively. $\Gamma(z)$ is the marine coastline at the horizon z, and λ is normal to the coastline.

It should be noted that, if spectral coefficients $A^i{}_n$ (t, z) have been obtained from the data, then tbe radionuclide concentration can be reconstructed for any point of the sea.

According to Danilov et al. (1996), the concentration of the ith radionuclide into the sea can be represented as follows:

$$b_h = \alpha\left(\vec{w}_{\perp} + y + s\right) b_q^h + \beta\left(\vec{w}_{\perp} + y + s\right) b_c^h \tag{4}$$

where α, β are the weight multipliers characterizing the contribution of various sources to the generation of the radionuclide field at point $\vec{x}_{\perp}$, z for time t ; $c^i{}_r$ is the concentration at the liquid boundary, $c^i{}_d$ is the contribution of other sources to the Black Sea radionuclide pollution, such as the atmosphere and the exchange through straits. Obviously, if $\left\{\vec{x}_{\perp}, z\right\}$ tends to $\left\{\vec{x}_{\perp}^{\,r}, z^r\right\}$, where $\vec{x}_{\perp}^{\,r}$ and z^r are any coordinates of the liquid boundary, then $\{\alpha, \beta\}$ must be equal to $\{1, 0\}$, respectively.

Therefore, our purpose is to reconstruct the field of radionuclide concentration in the sea and to find radionuclide fluxes through the following equations:

$$F_i = \oint_{S_r} c_r^i\, Q^r\, dS \tag{5}$$

where Q_r is the river transport, S_r the square of the cross–section of the river–bed at the mouth.

The principal variables and vectors used in the approach are shown in Figure 1.

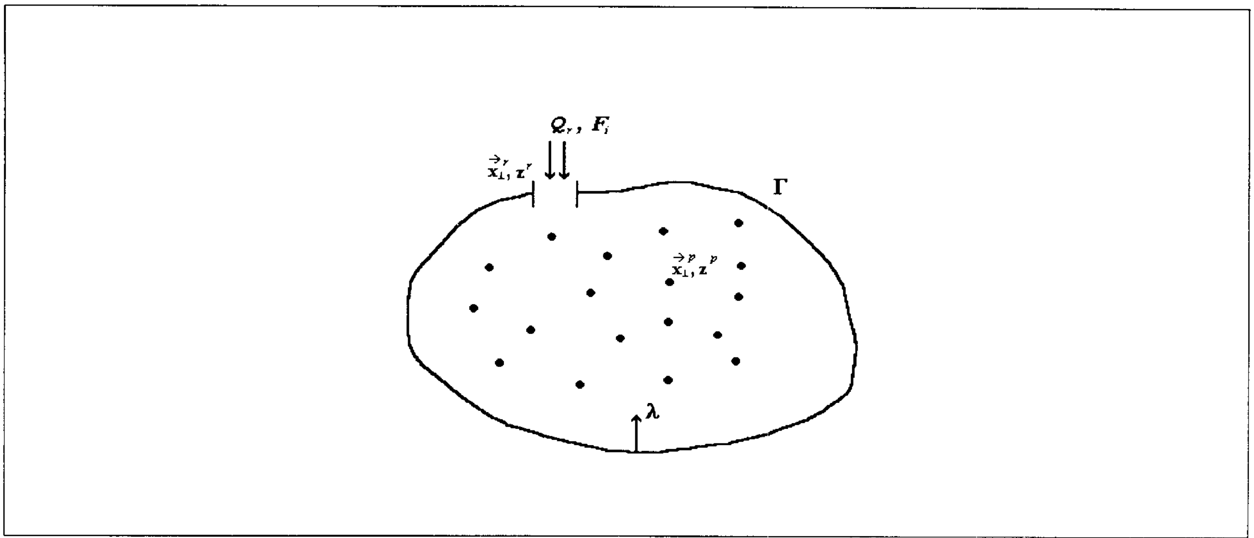

FIGURE 1. Variables and vectors. Dots indicate places where the concentrations of *i*th isotope were measured.

From the mathematical point of view, the problem indicated above can be reduced through a system of linear algebraic equations (see, Eremeev et al., 1994, 1995):

$$\sum_{n=1}^{N} A_n\left(t, z^p\right)\Psi_n\left(\vec{x}_\perp^p, z^p\right) = c^p + \delta c^p \tag{6}$$

where $\delta c\mathrm{P}_\mathrm{i}$ is the contribution of noise to the measured signal.

A special approach for the solution of similar systems has been developed by Ivanov and Margolina (1996), Eremeev et al. (1997) where special linear transformations were applied to reduce

the noise - useful signal ratio $\frac{\delta b^o}{b^o}$. Previously, the approach had been successfully used for the reconstruction of radionuclide fields in the Black Sea (Eremeev et al., 1994, 1995) and the Kara Sea (Danilov et al., 1996), and for the estimation of radionuclide balance of the White Sea (Danilov et al., 1997).

RECONSTRUCTED FLUXES OF DISSOLVED CS137 , CS134 AND SR90

The results of the reconstruction (mathematical aspects discussed above) are demonstrated in Figure 2, 3, and 4. It should be noted that the reconstructed monthly mean concentrations and fluxes regarding the Dnieper river was reduced by 10 times, because in the present study these characteristics may only be calculated for the outflow from the Dnieper - Bug liman. The reduction coefficient was obtained from the analyses of the data collected by Vakulovsky (1991).

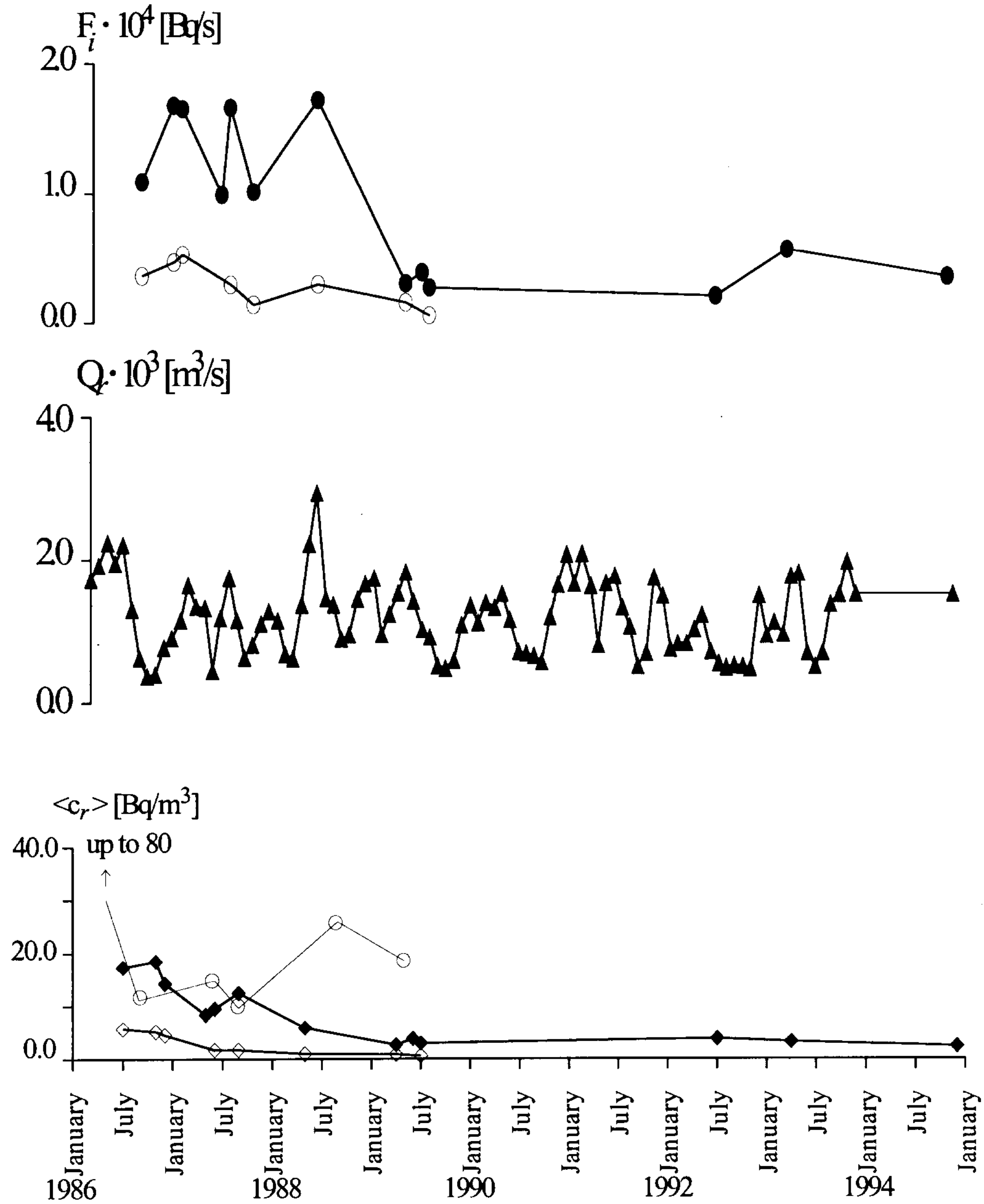

FIGURE 2. Reconstructed Dnieper fluxes of the dissolved Cs^{137} and Cs^{134}.The upper panel demonstrates the reconstructed fluxes of Cs^{137}(●)and Cs^{134} (o). The middle panel indicates the Dnieper water transport. The lower panel is the temporal evolution of mean monthly isotope concentrations for the Dnieper river. ◆ and o are the concentrations of Cs^{137} reconstructed in the present paper and measured by Vakulovsky et al. (1991), respectively. ◊ shows the concentration of Cs^{134} reconstructed in the present paper.

The principal conclusions of this study, regarding the riverine contribution to the post-Chernobyl Black Sea pollution and the estimation of the validity of the results, are listed below:

(i) The Dnieper and Danube rivers are not the principal contributors to the dissolved radionuclide levels in the Black Sea. For example, the dissolved radionuclide fluxes from the Bosphorus are larger than the summarized dissolved radionuclide fluxes delivered to the Black Sea by both the Dnieper and Danube Although these rivers have probably delivered significant amounts of radionuclide sorbed suspended sediment load to the Black Sea, such measurements have not been made in the suspended material. Individual contributions of these rivers to the Black Sea radionuclide balance will be discussed in more detail in the next sections. Here, we would like to indicate that over nine years the Dnieper has pumped into the Black Sea dissolved cesium equaling, approximately, $1.8 \cdot 10^{-3}$ PBq. A similar estimate for the Danube is $2.6 \cdot 10^{-2}$ PBq.

(ii) It may be noted from the temporal series analyses of cesium that the maximum mean monthly concentration determined at the river mouths occurs during the Fall (Figures 2, 3).

(ii) However, radionuclide fluxes reach their maximum values during the Spring. This is explained by the fact that in:

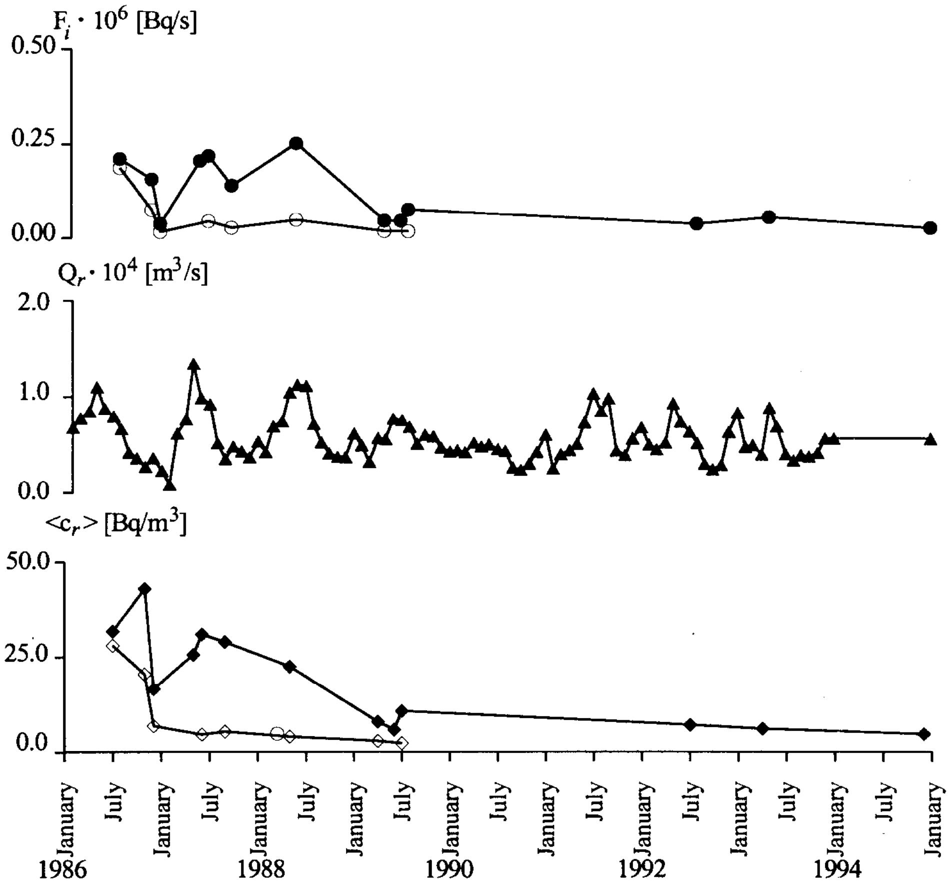

FIGURE 3. Reconstructed Danube fluxes of dissolved Cs^{137} and Cs^{134}. The upper panel demonstrates the reconstructed fluxes of Cs^{137} (●) and Cs^{134} (o). The middle panel indicates the Danube water transport. The lower panel shows the temporal evolution of monthly mean concentrations of Cs^{137} (◆) and Cs^{134} (◊) reconstructed in the present paper and the measured concentrations of Cs^{137} by *Kulebakina and Polikarpov* [1990] (o).

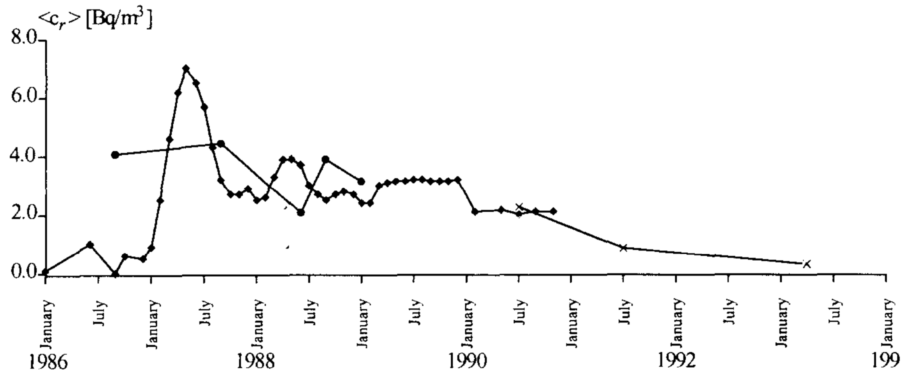

FIGURE 4. Reconstructed mean monthly concentrations of dissolved Sr^{90} for the Dnieper river.
◆ and ● are the measurements of *Polikarpov et al.* [1993] and *Vakulovsky et al.* [1991], respectively.
X shows the results of the present reconstruction.

During Fall, radionuclides are washed out from the soil by the rain water, whereas in Spring, the radionuclide fluxes are generated by the spring floods due to melted water. It was demonstrated by Borzilov et al. (1988) that the coefficient of radionuclide wash-out from the soil by rain water is considerably larger than the radionuclides pumped into the rivers by the snow melted water.

(iii) The validity of the results obtained was estimated through a comparison between the numerical results and the direct measurements of Vakulovsky [1991], Medinetz et al. (1992), Polikarpov et al. (1993) (Figures 2-4). The analysis of this comparison shows a good match between calculated and measured results.

RADIONUCLIDE BALANCE OF DISSOLVED CS137 IN THE BLACK SEA IN NOVEMBER 1986 AND JULY 1992

Let us estimate the cesium radionuclide balance for the Black Sea from the results of reconstruction discussed above. The total amount of dissolved Cs^{137} in the Black Sea for November 1986 (Q_1) and July 1992 (Q_2) was formerly calculated by Eremeev et al [1995] as equal to 2.8 PBq and 0.82 PBq, respectively. The result of the present study was demonstrated in November 1986 and July 1992, when the Dnieper river pumped into the Black Sea $5.7 \cdot 10^{-5}$ and $8 \cdot 10^{-6}$ Pbq, respectively. There were similar estimations for the Danube: $5.1 \cdot 10^{-4}$ PBq and $1.5 \cdot 10^{-4}$ PBq.

The maximum possible reduction of Q_2 due to the Bosphorus outflow can be calculated by the formula:

$$\Delta Q^k \approx Q_B \, c^k{}_{max} \qquad (7)$$

Here, Q_B is the mean monthly Bosphorus outflow, and c_{max} the maximum concentration of Cs^{137} in the upper 30–m layer of the Black Sea; symbols k = 1, 2 correspond to November 1986 and July 1992, respectively. For the Black Sea, the following numbers were used: $Q_B = 30 - 50$ km^3 month^{-1} The minimum estimation of Q_B is given in *Hydrometeorology and Hydrochemistry of Seas in the USSR (Black Sea)* (1991), and the maximum estimate is discussed by Murray et al. (1991); c^1 = 150 Bq·m^{-3}; c^2 = 38 Bq·m^{-3}, which follows our estimates of Eremeev et al. (1994, 1995).

Substituting these parameters in formula (7) gives:

$$\Delta Q_1{}^1 = 4.5 - 7.5 \cdot 10^{-3} \text{ PBq, and}$$
$$\Delta Q_1{}^2 = 1.1 - 1.9 \cdot 10^{-3} \text{ PBq.}$$

Using the established decay period of 30 years for Cs^{137}, it can be easily computed that this isotope would be reduced in radioecological balance approximately by $7 \cdot 10^{-3}$ PBq in November 1986, and by $1.8 \cdot 10^{-3}$ PBq in July.

To estimate the amount of Cs^{137} absorbed by marine organisms, the following Eremeev et al's formula was used:

$$\Delta Q_2^k = c_{\max} \sum_i K_H^i V \, Bm^i \qquad (8)$$

Here, K_H^i is the coefficient of radionuclide accumulation of the *i*th component of the marine biota, and Bm^i is the biomass of the *i*th biota component; V is the biomass. The maximum values of K_H^i characteristic of the Black Sea phytoplankton, are approximately equal to 10–11.5 per unit mass (Eremeev et al., 1993). These multi-annual estimates are given for the brown seaweed. The phytoplankton biomass for the Black Sea upper 1–m layer equal, approximately 110–160 mg – m^{-3} according to Pitsik (1971), and the volume of this layer is $4.15 \cdot 10^{13}$ m^3 . Therefore, $\Delta Q_2{}^1$ is less than $3 \cdot 10^{-5}$ PBq, for November 1986, and $7 \cdot 10^{-6}$ PBq, for July 1992, respectively. Consequently, the role of the marine biota in the reduction of dissolved Cs^{137} cannot be very important.

The bottom sediments play a considerable role in the reduction of Q. The results of the investigations discussed in Polikarpov and Lazorenko's (1992) studies indicate that on the shelf, muds accumulate approximately 10% of the dissolved Cs^{137}. Taking into account the factors of radio-capability for the different domains of the Black Sea estimated in this above-referred paper, we have calculated that the amount of $1 \cdot 10^{-2}$ PBq and $3 \cdot 10^{-3}$-PBq, respectively.

Summarizing the results discussed above, we come to the following conclusion: in 1986 the principal contributor to the generation of the Black Sea radionuclide field was the atmosphere. Then the considerable reduction of cesium activity was governed by the Bosphorus outflow, the accumulation of radionuclides by sediments and by the natural decay of isotopes. Therefore, the joint contribution of the Dnieper and Danube rivers to amount of the dissolved Cs^{137} and Cs^{134} budget of the Black Sea, during 1986–1992, was small and it may neglected in the terms of global estimation of the Black Sea radionuclide pollution.

TABLE 2. Amount of Cs^{137} (Bq/kg) in the sediments of the northwestern shelf of the Black Sea (Batrakov et al, 1997).

		Depth below sea floor (cm)							
Station coordinate and date of measurements		0 – 5	5 – 10	10 – 15	15 – 20	20 – 25	25 – 30	30 – 40	40 – 50
φ = 46°20′ λ = 31°14′	May, 1992	90	70	156					
	May, 1994	15							
φ = 46°20′ λ = 30°45′	May, 1992	89	95	61	6				
	May, 1994	150	29	65	30	13	5		
φ = 46°35′ λ = 31°45′	May, 1992	32	37 [1]		32	29	38		
	May, 1994	147	150	141	150	161	133	29	
φ = 46°32′ λ = 32°06′	May, 1992	1170	745	285	140				
	May, 1994	85	90	150	110	90	40	20	40
φ = 44°45′ λ = 33°32′	November 22, 1993	441	42						
φ = 45°00′ λ = 33°15′		49 [2]		0					
φ = 44°50′ λ = 31°15′		163	11	0					

[1] and [2] are the measurements in layers 5 – 15 cm and 0 – 10 cm, respectively.

Cs^{137} IN THE NORTHWESTERN BLACK SEA SHELF SEDIMENTS

It is clear from the above data that the shelf sediments accumulate a considerable amount of radionuclides. Therefore, it is important to estimate the amount of cesium which have been accumulating in the northwestern shelf sediments, and to define trends in the evolution of this process. It should be noted, however, that the problem of isotope transport by the suspended particulate matters will not be discussed here since there are no direct measurements of isotopes in such materials, as pointed out earlier.

The data collected by Batrakov et al. (1997), Ryabinin et al. (1995), Medinetz et al. (1992) and Piescu et al. (1997) will be used for this purpose in the present study. These data were collected in the Dnieper - Bug liman, in the north shallow part of the northwestern shelf and along the Romanian coast of the Black Sea. The principal conclusions derived from the analysis of these data can be listed as follows:

(i) There is not any obvious increasing trend regarding the depth of radionuclide activity in the shallow sediment column of the Black Sea. This is most probably due to the rapid transport of sediments from the shallow shelf areas into deep sections of the Black Sea.

(ii) Cs^{137} is observed in sediments even at depths of 1-1.2 m. For example, the concentration of these radionuclides measured by Ryabinin et al. (1993) in this Dnieper - Bug liman for July, 1992 were approximately equal to 10–20 $Bq \cdot kg^{-1}$. This isotope is clearly a Chernobyl effect. However, there is a considerable variability of radionuclide concentrations due, in our opinion, to the mixing of sediments delivered by the rivers with the sediments of the pre-Chernobyl period.

(iii) The data set also demonstrates the presence of considerable variations in cesium concentrations in the upper sedimentary layer (Table 2). In our opinion, this behaviour of the connected cesium can be explained by the resuspension of the upper layer as a consequence of storms, wind waves and bioturbation.

(iv) The cyclic variation in spatial distribution of the cesium concentrations is obvious in the shallow sediments of the Black Sea. The places where the concentrations are anomalously high (up to 1000 $Bq{\cdot}kg^{-1}$) alternate with areas of relatively low concentrations (10–15 $Bq{\cdot}kg^{-1}$).

Unfortunately, there is no possibility at present neither to separate the contributions of different factors to the pollution of the Black Sea bottom sediments nor to provide quantitative characteristics of such pollution, because of the lack of appropriate data.

CONCLUSIONS

The basic conclusions concerning the role played by the Dnieper and Danube rivers in the global pollution of the Black Sea can be outlined as follows:

1. The joint contribution of dissolved Cs^{137}, Cs^{134} and Sr^{90}, delivered by the Dnieper and the Danube to the Black Sea radionuclide pollution is several orders less than the atmospheric input in 1986, when the Chernobyl accident caused the transfer of considerable activity to the Black Sea via the atmosphere.

2. The results of the present study do not confirm the monotonous accumulation of radionuclide activity in the northwestern shelf sediments. The deposited cesium has a very complex behaviour and presently, a simple prediction of isotope accumulation in sediments is not practically possible.

In our opinion, there is a specific self-refining process operating in the Black Sea water column, concerning the Chernobyl radionuclides. The radionuclide amounts in the seawater have been reduced by the natural decay process, by export via the Bosphorous Strait, and by accumulation in the Black Sea sediments. For example, only for the five-year period (1986- 1992), shelf sediments accumulated an activity approximately equal to 0.93-1 PBq (Eremeev et al., 1995). The isotopes incorporated into the sediments and suspended particulate matters are transported from the shallow Black Sea shelf to the deep section of the basin, where they are not hazardous to the marine ecosystem. A quantitative estimate of the rate of this transportation should be made in the near future, by joint radioecological/geological studies.

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AN ASSESSMENT OF NITROGEN, PHOSPHORUS AND ORGANIC CARBON INPUTS TO THE BLACK SEA

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ABSTRACT

Riverine inputs are critical for the Black Sea ecosystem since they include considerable amounts of toxic substances and pollutants. Nutrient and organic matter inputs are especially important in relation to their role in the serious eutrophication problem of the Black Sea ecosystem. Among all inputs from various sources - including, those from the Bosphorus and Kerch straits, industrial and domestic waste discharges and atmospheric inputs - the riverine transport is known to be the major pathway of nutrient and organic matter towards the Black Sea.

Among all the rivers discharging into the Black Sea, the river Danube has the greatest loads, transporting >80% of the total riverine inputs of BOD5, total phosphorus (T'P) and total nitrogen (TN). On the other hand, the annual load estimates related to the Danube are highly variable, being in the range $2.3\text{-}13.6\times10^5$ tons TN and $3.5\text{-}6.0\times10^4$ tons TP. Compared to inputs from all the international rivers, the inputs of national rivers of all the riparian countries constitute less than 6% of the total riverine inputs to the basin. The input of Turkish rivers constitutes over 50% of all the national rivers and thus amounts to about 3% of the total load.

The transport of material by the lower layer current of the Bosphorus Strait to the intermediate depths of the Black Sea is also significant, its amounts being comparable to those of domestic and industrial waste discharges in terms of total organic carbon (TOC) and total phosphorus (TP). On the other hand, the material exported from the Black Sea to the Sea of Marmara by the upper layer current compensates the TP input, but exceeds the amounts of the total nitrogen (TN) and TOC inputs by the lower-layer current to the Black Sea. This net export of TN and TOC to the Marmara Sea has a detrimental effect on the Marmara ecosystem. In view of the scarcity of data, the total dissolved inorganic nitrogen (NH_4+NO_3+NO_2) is the only basis of any comparison between the atmospheric, riverine (mainly Danube) and Bosphorus Strait inputs at present. The atmospheric flux of total dissolved inorganic nitrogen estimated from the $N0_3$+NO_2 load given by Kubilay *et al.* (1995) is 0.9×10^5 t yr^{-1}. The corresponding inputs via the Bosphorus Strait and the Danube are 0.4×10^5 t y^{-1} (Polat and TugrW, 1996) and 3.4×10^5 (Mee, 1992), respectively. A comparison of these inputs shows the importance of the atmospheric nutrient flux to the Black Sea which at least constitutes 20 % of the total anthropogenic nutrient loads.

INTRODUCTION

The scientists vigorously recognize the uniqueness of the Black Sea among all other enclosed seas in the world. The interest has grown during the last decade as the Black Sea has been under an intense pollution and ecological damage (Mee, 1992; Kideys, 1994; Cociasu *et al.*, 1996, Kovalev *et al.*, 1997; Mikaelyan, 1997; Konsulov and Kamburska, 1997). However, the questions about the most important source of pollution (river inputs, atmospheric fallout or the unevenly distributed non-point sources around the Black Sea), the owner of the worst effect and the best strategy for cleanup have still been under discussion.

During the last three decades, the anthropogenic nutrient inputs to the world seas; especially to the coastal areas have increased dramatically (Bennekom and Salomons, 1981, Meybeck, 1982). This uneven distribution of nitrogen, phosphorus and organic carbon inputs are mainly of riverine origin and, together with the point and non-point sources surrounding the coastal areas they induced a widespread eutrophication problem in these waters (Ryther and Dunstan 1971, Smetacek, 1991). This has been especially reported for the northwestern shelf waters of the Black Sea (Bologa, 1985; Mee, 1992; Cociasu *et al.*, 1996) besides its other coastal waters and neighbouring seas, like the Azov Sea and the Sea of Marmara. For example, the Sea of Marmara has been adversely affected by the nutrient and organic matters from the rich northwestern shelf waters of the Black Sea (TuftW and Polat, 1995) which are advected by the rim current (Tolmazin, 1985-, Oguz *et al.*, 1992) and enter the Sea of Marmara through the Bosphorus Strait during most of the year (Sur *et al.* 1994).

The transboundary aspects of the environmental problems have forced the Black Sea countries to create regional action plans with cooperative work. The riparian countries signed the Bucharest Convention, aiming at protecting the Black Sea against pollution in 1992, which inspired the establishment of the Black Sea Environment Programme (1993) with the support of the Global Environmental Facilities (GEF). The Programme has covered the Black Sea Action Plan which, as a first level, lead to obtain the regional assessment of the land-based sources of pollution of the Black Sea, through the Activity Center on Routine Pollution Monitoring in Istanbul (Sankaya *et at,* 1997). Additionally, the Black Sea/Geographic Information System has been made available by GEF (Version 2, April 1997). At the second level of the Black Sea Action Plan, specific actions have been proposed to be achieved towards the end of the century, such as the assessment of inputs, negotiations on basin-wide strategy and on reduction of pollutants from international rivers and point sources. The international scientific research programmes (CoMSBlack, TU-Black Sea, EROS 2000) have also been initiated since the beginning of the 1990s.

The aim of the present study is to make a transboundary source assessment of the Black Sea. In making this assessment, attention is drawn to the difficulties associated with the uncertainties of the methods used for load estimations. The importance of some inputs up to now disregarded, such as the atmospheric deposition, is also discussed.

RIVERINE INPUTS TO THE BLACK SEA

When the riverine loads of dissolved and particulate forms of nutrients and organic material enter the marine environment, they are subject to pronounced chemical changes as well as they enter the food web. The main factors arising in the advection of nutrients and organic matter from rivers to the open sea was briefly defined by Bennekom and Salomons (1981), as the estuarine mixing during which the physico-chemical interactions between dissolved components and suspended material take place and the effect of sedimentation and mineralization processes in the sediments. These inter-related factors prevent the whole riverine load to reach the open waters, hence, the possible effects of them are more pronounced in coastal waters; like the northwestern shelf area of the Black Sea which is under the direct influence of highly polluted loads from major rivers of the Black Sea drainage area; mainly the Danube.

Sankaya *et al.* (1997) published a region-wide documentation of land-based sources of pollution for the Black Sea which has been limited to point sources of wastewater discharges (domestic, industrial) and to inputs through the rivers. Diffuse sources, surface runoff and atmospheric fallout have not been included in this assessment. The authors concluded that the total riverine inputs of nutrients and organic matter contribute 83-99% to the region-wide loads.

Table 1 gives a comparison of the loads of international rivers supplying the major inputs to the Black Sea, taking into account the contribution of national rivers. For example, the Turkish rivers, including the Yesilimak, Kizilirmak and Sakarya, provide more than 50% of the total load of all national rivers and about 3% of the total riverine inputs to the Black Sea (Sankaya *et al.* 1997). Çoruh (Chorokhi) was not included in Table I since it provides a very small contribution, compared to other international and the Turkish rivers. The nitrogen loads given for Dnieper, Dniester and the Turkish rivers,Yesukimark and Kizilimak, are in terms of Total Inorganic Nitrogen (TIN). One important feature of the given input values is that more than 80% of the total nitrogen, phosphorus and organic matter inputs to the Black Sea via the international rivers is discharged by the Danube. The TIN and

TP loads given by Mee (1992) and Cociasu *et al.* (1996, 1997) are considerably higher than the loads given (Table 2) by Sankaya *et al.* (1997). Cociasu *et al's.* (1996) estimates were based on the daily measurements of nutrients at the Sulina branch of the Danube and the water discharge measurements in the upstream between 1988 and 1992. The other estimates of the Danube nutrient loads given by Cociasu *et al.* (1997) comprise 1980-1995 data set. They are presented as annual averages in Table 2.

There is also a significant discrepancy between the estimates of the nutrient inputs via the Turkish rivers (Table 3). For example, total nitrogen and phosphorus loads given by Sankaya *et al.* (1997) are not at proportional levels of dissolved inorganic nutrients given by Balka* *et al.* (1990). The reason for this may be in the different sampling periods, frequencies and locations. Balka* *et al.* (1990) calculated the loads from the major Turkish rivers inputs (Yesilimak, Kizilimak and Sakarya) as an annual average from 1983 and 1984 measured concentration data and water discharges.

TABLE 1. Comparison between the nutrient loads of main international rivers and those of the Turkish rivers in tons y^{-1} (Sankaya et al. 1997).

	Danube	Dnieper	Dniester	Turkish
TN	229,181	11,180	22,750	12,730
TP	34,938	3,970	980	1,713
BOD	774,643	56,320	13,300	18,090

TABLE 2. Different nutrient input values given for Danube in tons y^{-1}.

	Sankaya et al'97	Mee '92	Cociasu et al.'96	Cociasu et al.'97
TIN		340,000	600,000-800,000	652,000
PO_4			23,000-32,000	18,000
TN	229,181			
TP	34,938	60,000		

TABLE 3. Nutrient and organic matter inputs from the Turkish Rivers to the Black Sea (tons y^{-1}).

	Sankaya et al.'97	Balkas et al.'90
TIN		24,599
PO_4		1,728
TN	12,730	
TP	1,713	
BOD	18,090	17,500

From the above discussion, it can be stated that a precise estimate of riverine inputs to the coastal waters needs an adequate sampling strategy representing the whole year; a long-term monitoring programme which can clarify the historical changes; and simultaneous measurements of water discharges and chemical concentrations.

INPUTS FROM THE BOUNDARIES

Inputs via the straits

The two straits - Bosphorus and Kerch - connect the large Black Sea basin to the neighbouring seas of Marmara and Azov. The Bosphorus Strait has a major importance for the Black Sea, since it represents the only connection to the open ocean waters able, to some extent, to ventilate the Black Sea by a sub-surface flow. On the other hand, the Black Sea is the major source of nutrients and organic carbon for the productive sea surface waters of the Marmara Sea (Tugrul and Polat, 1995) and even for the Mediterranean, via the Dardanelles (Polat and Tugrul, 1996).

Polat and Tugrul studied the exchange of phosphorus, nitrogen and organic carbon between the Black Sea and the Sea of Marmara via the Bosphorus (1995, 1996), using systematic data collected at the northern and southern exits of the strait during 1986-1994 (Table 4). The seasonal variations, vertical distribution of particulates and dissolved forms of both organic and inorganic fractions of nitrogen, phosphorus and organic carbon were discussed in these studies. The steady state of the annual water balance of the Sea of Marmara was used in the calculations. These studies show that there is a net outflux of TN and TOC from the Black Sea to the Marmara Sea, whereas the out- and influxes of TP balance each other. TIN (NH4+NO2+ N03-N) represents nearly 20% of the TN outflux from the Black Sea which is about 34,200 t y-1. This is balanced with the influx of the same fractions to the Black Sea which is about 40,000 tonsy^{-1} being 80% of the TN influx (Polat and Tugrul, 1995). Therefore, it can be concluded that there is no net influx of nutrients and organic carbon from the Marmara Sea to the Black Sea. Nevertheless, the annual inputs of total phosphorus, nitrogen and organic carbon to the Black Sea via the Bosphorus Strait are respectively around 9,000, 50,000 and 250,000 tons.

The extent of uncertainties in those input estimates depends on some episodic events, such as the blockage of the sub-surface flow (Ozsoy *et al.,* 1994), limited simultaneous measurements of currents and chemical concentrations. However, the chemical concentrations and the flow rate of sub-surface water currents are less variable during a year compared to the seasonal variability in the surface waters (Polat and Tugrul, 1995)

The available literature on the inputs via the Kerch Strait is quite limited. Sankaya *et al.* (1997) report a net annual influx of nitrogen and phosphorus from the Azov Sea to the Black Sea of 43,900 and 3,1 00 tons, respectively.

TABLE 4 The exchanges of phosphorus, nitrogen and organic carbon via the Bosphorus.

	TP	TN	TOC
(-)(1)	8,800	171,000	1,440,000
(-)(2)	9,800	171,000	1,430,000
(+)(1)	9,000	48,000	250,000
(+)(2)	9,000	51,000	240,000

(-) outflux from the Black Sea (tons y^{-1})
(+) influx into the Black Sea (tons y^{-1}).
(1) & (2) Polat and Tugrul, 1995 & 1996 respectively with the data sets 1986-1992 and 1986-1994.

Atmospheric input

The atmospheric deposition (wet+dry) of nutrients and organic matter on the coastal and open waters increases primary production. For example, atmospheric nitrogen loading stimulates the primary production of nitrogen in the limited coastal and offshore waters (Paerl, 1985, Paerl *et al.*, 1990). In recent years, some toxic and non-toxic phytoplankton blooms have been observed in the coastal waters under the direct influence of atmospheric nitrogen deposition (Paerl *et al.* 1990, Smetacek *et al.,* 1991, Paerl, 1995). The financial importance of atmospheric deposition on coastal nitrogen dynamics was thoroughly discussed by Paerl (1995), together with the techniques being deployed to trace the effects of this source and to come up with more realistic coastal water management strategies. At present, it is known that more than 10-50% of coastal nitrogen loading is attributed to atmospheric deposition (wet+dry) which has been generated globally in an uncontrolled manner over the past 4 decades (GESAMP, 1989; Loye-Pilot, 1991; Duce, 1991).

Data published on the atmospheric deposition of nutrients to the Black Sea is very limited. NO_3+NO_2 deposition (wet+dry) was reported as 44,100 t y^{-1} by Kubilay *et al.* (1995). On the other hand, Hacisalihoglu *et al.* (1992) estimated a NO_3 flux of 500,000 tons y^{-1} over the whole Black Sea, being of an order of magnitude higher than Kubilay *et al.'s* (1995) estimate. In both studies, ship-borne sampling was used and oxidized nitrogen compounds were measured in the water extracts of the aerosol samples. Data used in these studies have not been collected systematically enough to represent the whole year, thus producing inconsistencies between the two estimates.

The NH_4 loading over the Black Sea can be estimated in about the same amount of water soluble NO_3+NO_2 in aerosols which was given for the Western Mediterranean by Alarcon and Cruzado (1990). Hence, the deposition to the Black Sea of total dissolved inorganic nitrogen compounds associated with aerosols can be evaluated in about 90,000 t y^{-1} by using Kubilay *et al.'s* (1995) estimate.

COMPARISON BETWEEN INPUTS FROM DIFFERENT SOURCES

Although there are discrepancies between the input values estimated by different sources, a comparison of the loads from different sources is justified after the selection of the most realistic values and some necessary standardizations. Table 5 provides the basis for such a comparison.

The first column of Table 5 groups together the transboundary sources of material transported to the coastal and the offshore waters of the Black Sea. Domestic and industrial inputs from point sources along the Black Sea coastline were taken from the values given by Sankaya *et al.* (1997). However, the BOD_5 load has been converted to TOC load with a BOD_5:TOC ratio of 1.5 given by Benefield and Randall (1980) for domestic wastes. As this ratio may change considerably for different industries, a moderate value of 1.5 has also been accepted for the industrial inputs. The BOD_5 load given for international rivers has been converted to TOC using the stoichiometric relationship C:O_2=106:138 given by Redfield *et al* (1963) for the natural surface waters. The same relationship has been used to achieve the TOC estimate of the national rivers which has been based on the Turkish river inputs given in Table 3 which is multiplied by two to calculate the contribution of all national rivers in the Black Sea basin. The TP input of the international rivers was calculated from the Danube input given in Table 2 and the other major river inputs given in Table 1. The TP input by national rivers in Table 5 was calculated by multiplying the PO_4 load (1,728 tons y^{-1}) given in Table 3 for Turkish rivers by 2.5; a factor for the conversion of PO_4 in river waters to TP (Meybeck, 1982), and then taking twice this value to obtain the inputs from all national rivers in the Black Sea drainage area. Similarly, the TN input by international rivers has been estimated from the TIN values given for the Danube in Table 3, then multiplied with TN:TIN=1.7 ratio (Meybeck 1982) and added to the other major river inputs given in Table 1. The national river inputs of TN was estimated in a similar way as for the national rivers TP input.

The net input values via the Kerch Strait to the Black Sea reported by Sarikaya *et al.*(1997) was assumed to represent the total nutrient inputs. They are given in Table 5 together with the nutrient inputs via the Bosphorus Strait. It should be mentioned that the Bosphorus and Kerch inputs have been presented separately, since the Bosphorus inputs are given in gross values while the outputs from the Black Sea via the Bosphorus have been disregarded in the scope of the load comparison.

TABLE 5. The annual inputs of total organic carbon, nitrogen and phosphorus from various sources to the Black Sea Basin, in t y^{-1}

	TOC	TP	TN	TIN
Domestic+Industrial	102,252	8,675	140,629	340,000
International rivers	650,000	65,000	612,000	50,000
National rivers	27,000	8,600	85,000	40,800
Bosphorus	240,000	9,000	51,000	
Kerch		3,100	43,900	90,000
Atmospheric	Unknown	Unknown	Unknown	

Finally, the last column was arranged to compare the atmospheric TIN load to inputs ftom the other sources. The TIN input via the international rivers was presented by a moderate value of the Danube given by Mee (1992); the TIN input by national rivers represented about twice the Turkish river inputs given by Balka *et al.,* (1990), which is also an intermediate value among the published data. It can be concluded from this comparison that the atmospheric deposition is the second major source of nutrients into the Black Sea.

CONCLUSIONS

Before the achievement of specific actions for the whole basin on behalf of the Black Sea Action Plan by the Black Sea countries, it was considered essential to carry out a precise assessment of the land-based sources of pollution. With this goal, the Activity Center on Routine Pollution Monitoring in Istanbul published a pollution assessment report (Sankaya *et al.,* 1997). The report has to be taken seriously into account, since it contains valuable input data from the countries surrounding the Black Sea. The ideas contained in the present study have been supported and, on the basis of comparison of inputs from the various sources, the author concluded the following:

- The main source of nutrients and organic carbon inputs to the Black Sea is of riverine origin, mostly from international rivers.

- Compared to the other major rivers discharging to the Black Sea, the River Danube provides the more important contribution. However, there is a wide range of estimates regarding nutrient inputs. For example, N and P inputs 2-5 times higher have been reported for the River Danube by different authors.

- The importance of atmospheric nutrient inputs to the Black Sea had not been noticed until recently, creating a discontinuity in source assessment calculations.

- The riverine contribution of inputs for the whole region has been evaluated in 83-99% by Sarikaya *et al.,*1997; this estimate disregarded mainly the contribution of atmospheric inputs. The riverine inputs should be at a 70-75% level when the atmospheric contribution has been regarded as 20% of the total which, in reality, may be accepted as a minimum estimate.

The discussions throughout the text and the above-mentioned observations lead us to the conclusion that it is necessary to develop a common calculation methodology between the riparian countries for estimating the loads before deciding how to reduce them. The choice of parameters and time and space resolution in sampling should be carefully established in order to ensure an accurate level of input data on nutrients and to obtain useful data for the calculation of long-range transboundary marine pollution atmospheric deposition, and accuracy in riverine transport calculations. Daily data on water and nutrient to be collected at some hot spots and intercalibration exercises in the meantime will also enhance the quality of the land-based input data.

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PRELIMINARY ESTIMATE OF DISSOLVED FE, MN AND PB FLUXES THROUGH THE BOSPHORUS STRAIT

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ABSTRACT

In this study, the systematic total dissolved Fe, Mn and Pb data at the Black Sea and Marmara Sea exits of the Bosphorus Strait have been presented; they are used for the estimation of metal exchange fluxes between both seas. The data were obtained during a one-year period, from February 1996 to January 1997 in the course of a Water Quality Monitoring Project supported by the

Municipality of Istanbul. The estimation of out-fluxes of total dissolved Fe, Mn and Pb at the Black Sea surface gives respectively 16185, 1090 and 215 tons/y, that is to say 2-5 times larger than the export from the Marmara Sea to the Black Sea. The concentration ranges were 6-120 μg Fe/L, 1-63 μg Mn/L and 0.8-3.3 μg Pb/L in the water surface layer of the Black Sea outflow, and 11.3-30 μg Fe/L, 1-12 μg Mn/L, 0.8-2.3 μg Pb/L in the lower-layer waters of the Marmara Sea inflow.

INTRODUCTION

The Bosphorus Strait is a narrow, shallow (sill depth: 35 m) and ~30 km long channel with a two-layer flow regime between the Black Sea and Marmara Sea. The upper-layer waters with an average salinity of 17-18 ppt is 45-50 m thick at the Black Sea exit, but gets thinner (15-20 m) and more saline (~20 ppt) at the Marmara Sea exit. More saline (>30 ppt) lower-layer waters of Mediterranean origin flows from south to north spreading from a thin (~10-15 m) bottom layer at the Black Sea exit to the intermediate depths in the Black Sea. The hydrography, flow exchange, mixing processes and the sea-level data in the Bosphorus have been discussed in previous studies by using the long-term physical data (Ünlüata et al., 1990; Özsoy et al., 1986-1994; Özsoy et al., 1995, 1996; Latif et al.,1991; Yüce,1993, 1986 and Alpar, 1994, Büyükay,1989). Modeling studies on the exchange flows related with hydrography in the Bosphorus Strait are also available (Oğuz et al., 1990; Johns and Oğuz, 1990).

The northwestern shelf waters of the Black Sea are heavily polluted by rivers inputs (mainly by the Danube) and wastewater discharges. These polluted waters reach the Bosphorus exit through the alongshore currents and enter the Marmara Sea (Sur et al., 1994), thereby adversely effecting the Marmara Sea ecosystem (Kocataş et al., 1990; Polat and Tuğrul, 1995; Tuğrul and Polat, 1995). In addition to the pollutant inputs from the Black Sea, the Marmara Sea also receives significant amounts of domestic and industrial inputs from the İstanbul Metropolitan Area (IMA) (Tuğrul and Polat, 1995). 15% of the population and about 40% of the industry of Turkey are implanted in this area (Orhon *et al.*, 1994. Moreover, the maritime traffic through the Bosphorus Strait and the tanker accidents further contribute to the environmental problems of the Marmara Sea.

Trace metals of both anthropogenic and natural origin are found in various forms in the marine environment. Total dissolved (including the colloidal fraction) and associated metal concentrations of suspended matter in the coastal waters generally change dynamically in time and space, compared to those in the sediment and biota. Tappin *et al.*, (1993) summarized the major processes controlling the behavior of dissolved trace metals in coastal waters, such as mixing of fresh and saline waters, contribution from the anoxic shelf sediments and removal by planktonic organisms.

In this study, we present the first systematic total dissolved Fe, Mn and Pb data from the Marmara Sea and Black Sea exit regions of the Bosphorus Strait. Based on these data, we have estimated the heavy metal fluxes exchanged with the upper and lower layer currents through the Bosphorus Strait. The Municipality of Istanbul obtained the physical and chemical data during February 1996-January 1997 in the course of a Water Quality Monitoring Project supported.

MATERIALS AND METHODS

The monitoring project involved sampling and measurements at 12 stations as a whole, four of which being sampled monthly (K0, B13, B7, B2) by R/V Arar and all 12 stations on a seasonally basis (Figure 1). All the sampling stations have shallow water depths (<100 m), except station M23 where the water depth is >1000 m. The sampling depths were chosen at 0.5m, 5m and then at 10m interval until the bottom. Here, we only use the monthly and seasonal data, respectively collected at Stations K0 and M8 (Fig. 1) for the estimation of metal exchange fluxes through the Bosphorus Strait.

All the samples were collected with 5L Niskin bottles. 1 L of seawater was filtered through 0.45 µm membrane filters pre-washed with 1 N HNO_3. Dissolved metals were concentrated from 500-ml sea water samples using a modified version of the dithiocarbamate/chloroform organic extraction technique developed by Bruland et al. (1979). The sample was oxidized with two separate 2-ml additions of concentrated Q-HNO_3, re-dissolved in 1M Q-HNO_3. The back extraction step was omitted, and the two-chloroform extraction steps were evaporated to dryness in a quartz beaker and analyzed by flame mode atomic absorption spectrophotometry. The precision and the detection limits of the analytical method are given in Table 1. The detection limits are high but, the precision and accuracy of the method are more than satisfactory, with 94 % of Fe, 78% of Mn and 71% of Pb data collected being above the detection limits (Table 2). The blank values given in Table 1 show the procedural blanks. The reagent and instrument blanks have been subtracted from the sample and procedural blank concentrations during the measurements.

TOTAL DISSOLVED METAL FLUXES BETWEEN THE BLACK SEA AND THE SEA OF MARMARA

The annual out-fluxes of total dissolved trace metals from the Black Sea to the Sea of Marmara have been calculated from the average surface layer concentrations at Station K0 which was sampled monthly. The salinity profiles at Station K0 show that the upper layer waters extend to about 40-m deep during the whole year (Fig. 2). The depth-integrated metal concentrations in this layer (0-40 m) are used to calculate the monthly averages. The annual means were calculated from the monthly averages given in Table 2. The influxes to the Black Sea with the Bosphorus sub-surface flow have been calculated from the concentration measured at station M8 where the subsurface waters extend from about 30m down to the bottom (Fig.3). The depth integrated metal values of 40-60 m (salinity>38.5) are accepted as seasonal averages, and the annual means for each metal concentration were calculated from these values (Table 2). The annual mean concentrations were consequently corrected on the basis of the procedural blank values, and used in flux calculations.

The fluxes of water volume have been estimated by Özsoy *et al.*, (1995) taking into account the evaluation of long-term salinity data in the region. Their calculations are principally based on the steady assumption that the water exchange of fluxes is constant, on a yearly time scale; giving 562 (Q_{bu}) and 263 (Q_{bL}) km^3/y of net water exchange respectively for the surface of the Black Sea and the sub-surface of the Marmara Sea flows (Fig. 4). The vertical exchanges through the Bosphorus Strait due to mixing have been subtracted from the lateral volume fluxes to obtain the net values. The annual total trace metal out- and in-fluxes from and into the Black Sea were calculated with the following equations used in the steady state model water exchanges during a year, which was previously used by Polat and Tuğrul (1995, 1996) for the estimation of nutrient fluxes.

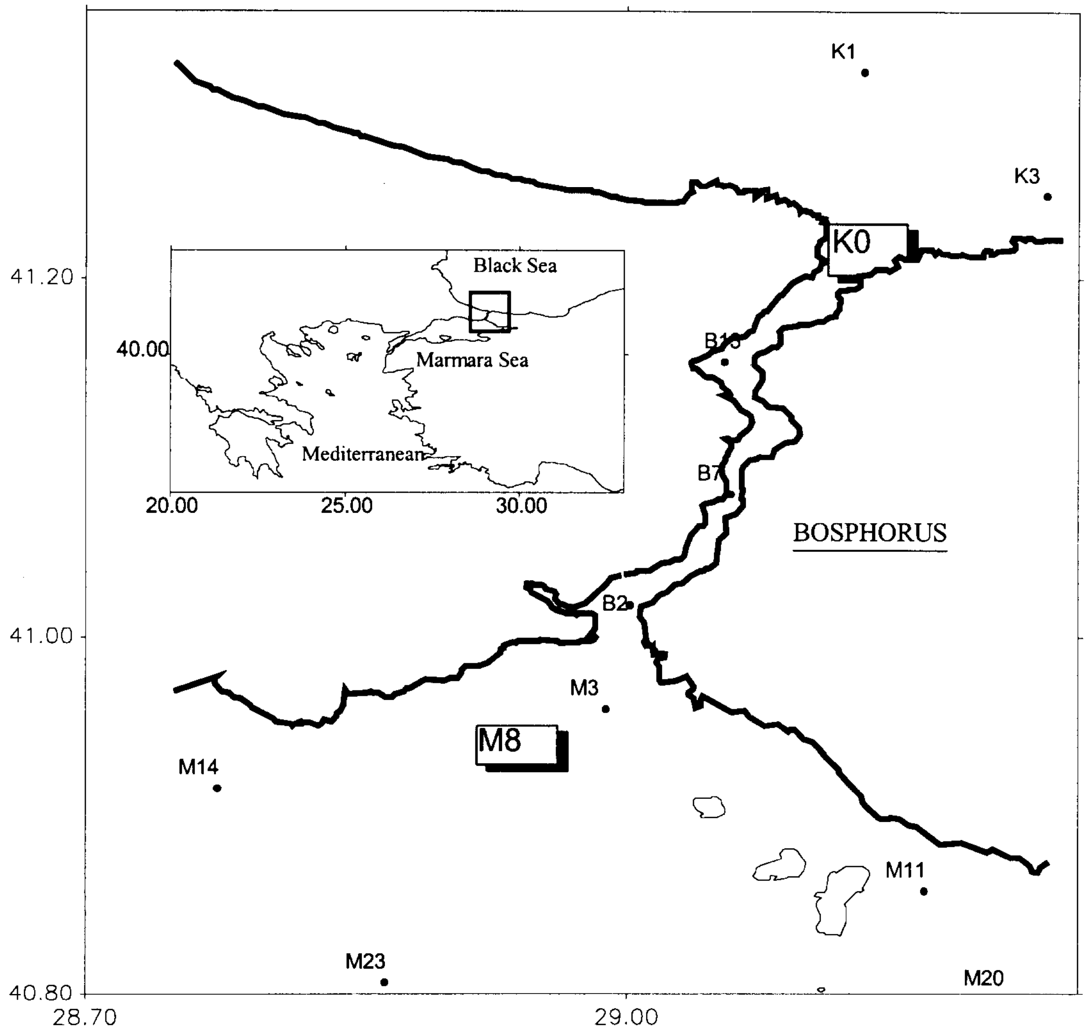

FIGURE 1. The location of the study site and the sampling stations.

TABLE 1. Analytic method criteria

Elements	Blank (µg/L) (n=20)	3σ	Precision (n=20)	Detection Limits (nM)	Detection Limits (µg/L)
Fe	n.d*	-	12	71	4.0
Mn	1	0.63	13	18	1.0
Pb	0.81	1.10	23	4	0.8

* n.d: non detection

TABLE 2. Depth-integrated average concentrations (µg/L) of total dissolved trace metals at stations K0 (0.5-40 m) and M8 (40-60 m). BDL:below detection limits.

	Fe	M n	Pb
February-96 K0	60.5	6.68	1.00
(M8)	4.0	1.00	0.80
March (K0)	51.5	BDL	BDL
April (K0)	47.5	2.12	BDL
May (K0)	13.3	1.83	BDL
(M8)	21.0	2.60	0.85
June (K0)	1 9.5	1.41	0.98
July (K0)	21.7	3.26	BDL
August (K0)	18.5	7.51	1.02
(M8)	13.5	10.00	1.65
September (K0)	17.5	2.64	1.21
October (K0)	19.8	1.80	0.88
November (K0)	25.7	1.58	1.58
(M8)	11.5	1.10	0.90
December (K0)	30.2	1.24	1.28
January -97 (K0)	19.8	2.26	1.19
x±s (n=12) C_1	28.8±15.5	2.94±2.04	1.18±0.20
(n=4) C_2	12.5±6.1	3.65±3.72	1.05±0.35

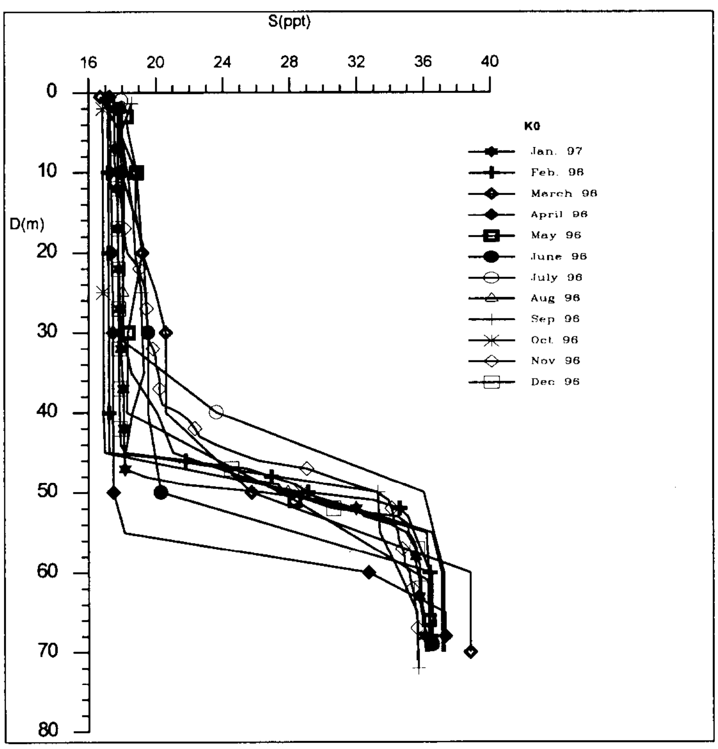

FIGURE 2. Monthly salinity profiles at station K0 during February1996 January 1997.

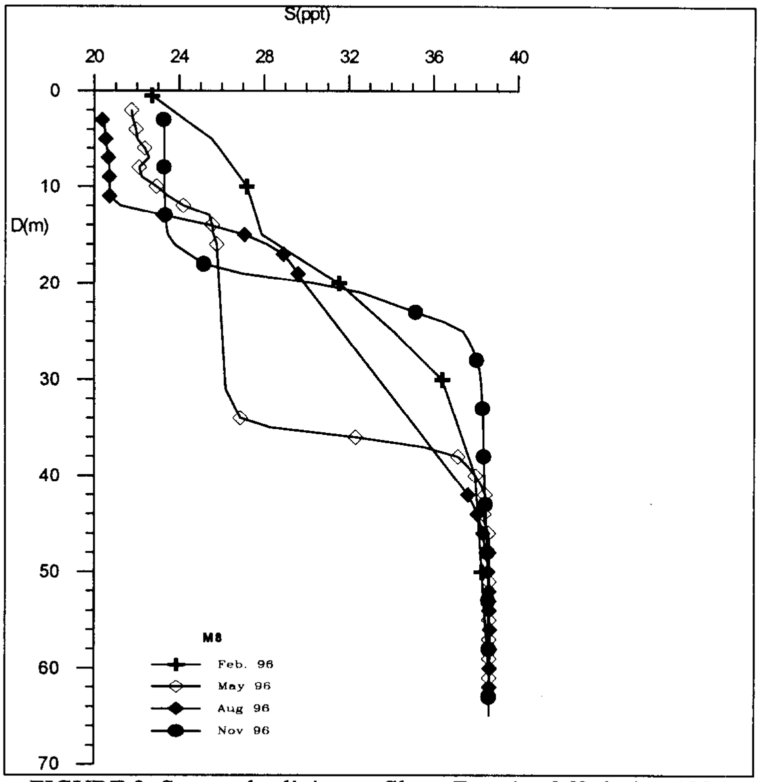

FIGURE 3. Seasonal salinity profiles atF station M8 during 1996.

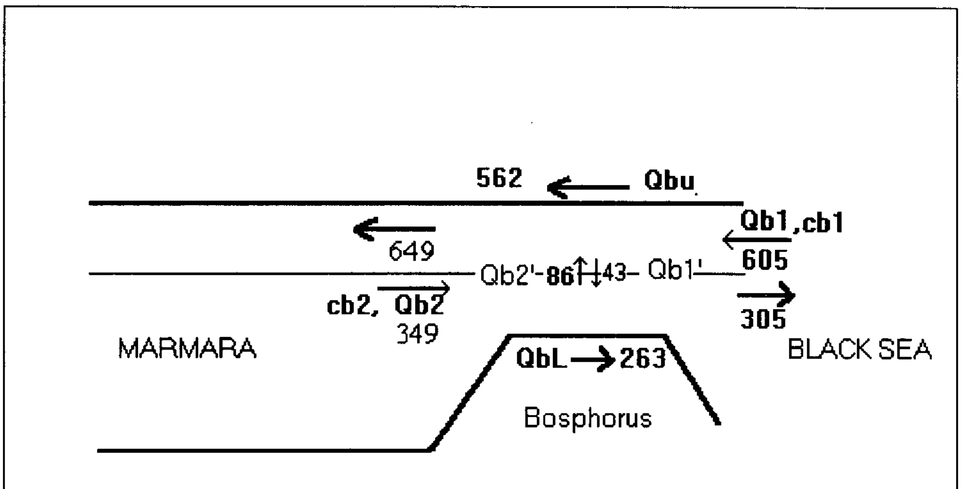

FIGURE 4. Water fluxes (km/y) Bosphorus Strait (after Özsoy et al., 1995).

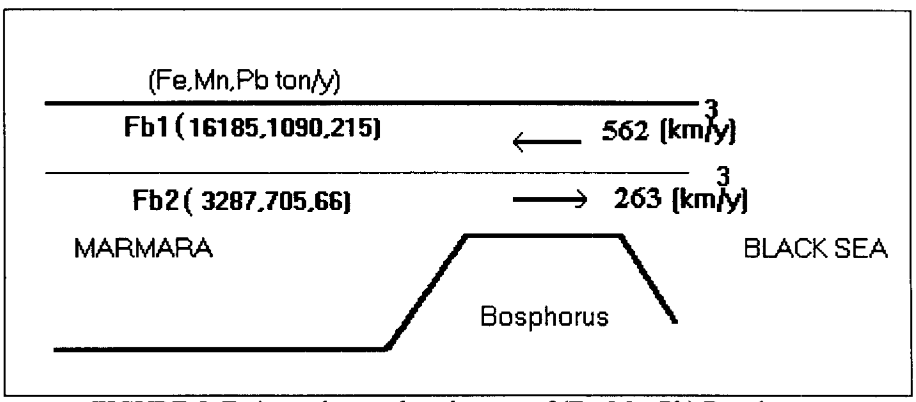

FIGURE 5. Estimated annual exchanges of (Fe, Mn, Pb) Bosphorus.

Surface Black Sea outflux (F_{b1}) = Q_{bu}* C_1 ; Q_{bu}= Q_{b1}-$Q_{b1'}$.
Sub-surface Marmara outflux (F_{b2})= Q_{bL}* C_2 ; Q_{bL}= Q_{b2}-$Q_{b2'}$.
Where:
F_{b1} , F_{b2}: Annual metal fluxes
C_1 : Annual mean metal concentration (K0)
C_2: Seasonal mean metal concentration (M8)
Q_{bu},: Net lateral water outflux from the Black Sea
Q_{bL} : Net lateral water influx into the Black Sea
Q_{b1}, Q_{b2}: Lateral water fluxes at the Bosphorus exits
$Q_{b1'}$, $Q_{b2'}$: Water fluxes through the Bosphorus due to vertical mixing.

The Black Sea surface outfluxes of total dissolved metals are calculated as 16185 tons Fe/y, 1090 tons Mn/y and 215 tons Pb/y and those for the Marmara sub-surface outflux as 3287 tons Fe/y, 705 tons Mn/y and 66 tons ton Pb/y (Fig. 5). Thus, the export of total dissolved trace metals from the Black Sea to the Marmara Sea is 2-5 times larger than the export from the Marmara to the Black Sea. This is mainly due to the larger annual flux volume of the surface Black Sea flow compared to the sub-surface Marmara Sea flow. The mean concentration values at the two exits are not significantly different (Table 2), except for Fe; dissolved Fe is much higher in the upper-layer because of the high input of Fe-rich river waters into the Black Sea.

Although the systematic trace metal data obtained during one-year period is insufficient to estimate the average annual fluxes to the Black and Marmara Seas via the Bosphorus Strait, we believe that the monthly data at Station K0 can safely be used to report the order of magnitude of trace metal export from the Black Sea to the Marmara Sea with the upper layer current. However, the amount of trace metal exported from the Marmara Sea to the Black Sea, computed from the seasonal data at station M8, should be taken tentatively and used only for comparison with the out-fluxes from the Black Sea.

DISCUSSION

In this study, only monthly average and annual mean values have been used throughout the text, without any details about seasonal changes, since the sampling period is not long enough to discuss the seasonal variability of trace metal concentrations. The ranges of annual concentrations of total dissolved trace metals in discrete surface layer depths at Station K0 were 6-120 μg/L Fe, 1-63 μg/L Mn and 0.8-3.3 μg/L Pb and 11.3-30 μg/L Fe, 1-12 μg/L Mn, 0.8-2.3 μg/L Pb in the lower-layer water at Station M8. Additionally, the flux estimations reported here should be taken cautiously; they have to be accepted as first rough approximations. However, the project has been going on and the particle-adsorbed metal fractions are also being measured. Therefore, there is hope that it will be possible in the future to make more accurate flux estimations together with an enhanced discussion on seasonal variations of both dissolved and particle-adsorbed fractions.

To make a transboundary source assessment in the Black Sea, the atmospheric and riverine inputs and influxes from the adjacent seas (Marmara Sea and Azov Sea) mainly, should be evaluated together. The trace metal inputs via the atmospheric (wet+dry) deposition have been estimated by Hacısalihoğlu et al. (1992) in 139000 tons Fe/y, 6800 tons Mn/y, 3900 tons Pb/y. The atmospheric Pb input was also reported by Kubilay et al. (1995) in 1740 tons/y. On the other hand, the riverine inputs were reported as 8400000 tons Fe/y, 144000 tons Mn/y (Hacısalihoğlu et al., 1992). The Pb input was only reported for the Danube as 4500 ton /y (Mee, 1992). These studies have not been carried out in the framework of monitoring Programmes and the sampling was done in short periods, seasonally or during certain months only. Furthermore, the flux estimates only give us the direct discharges into the Black Sea and do not consider the residence times in the seawater. Other complications in the transboundary source assessment are the insufficiency of the atmospheric and riverine input data on the trace metals and the absence of any data on the metal contribution due to antifowling used for ship painting. Additionally, data related to the inputs via the Kerch Strait from the Azov Sea could not be obtained from the literature. All these shortcomings show that our data is only meaningful for the estimation of Fe, Mn, and Pb inputs and outputs to and from the Black Sea via the Bosphorus Strait, and that a comparison to contributions from the other sources is not possible at the moment.

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POLLUTION OF THE BLACK SEA SURFACE BY ATMOSPHERIC AEROSOLS

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ABSTRACT

In this presentation, some aspects of the pollution of the Black Sea by atmospheric aerosols have been analyzed. It is concluded that the main pollution of the Black Sea via the atmosphere is due to anthropogenic factors. It is shown that the Eastern Black Sea annually receives 0.7-1.58 t of solid aerosols, 0.47-1.02 t of sulphur compounds, 14.6-56.2 t of carbon oxide and 0.1-0.22 t of nitrogen oxide.

INTRODUCTION

Aerosols enter the atmosphere either from the surface of the earth, or from the cosmic space. Long residing atmospheric aerosols in particular, have a cosmic origin. These particles are captured by air currents and, owing to stratospheric circulation processes, they quickly disperse throughout the huge air space surrounding the Earth. The movement of these particles towards the earth surface occurs slowly and directly depends on the structure of the vertical stratification of the free atmosphere. The troposphere constitutes a particularly strong obstructing factor, always overlaid by a high concentration of aerosol particles layer - so called "Junge layer". It is noteworthy that aerosols of cosmic origin do not represent at all the only source of pollution of this layer. Strong volcanic eruptions and forest fires strew in large quantities of aerosol particles at high latitudes in the atmosphere, which mainly form a high concentration zone in the lower atmospheric layers. There is no basis for considering that the concentration of aerosol particles in the stratosphere of both cosmic and natural terrestrial origin tends to change with the time. They represent permanent sources of pollution for the underlying surface, and hardly can change the level of sea surface pollution.

Tropospheric aerosols are the main pollutants of the underlying surfaces. Their increasing anthropogenic influence on the environment, particularly with the rapid industrial development, has caused the accumulation of hazardous aerosol particles in the troposphere. Their distribution in the troposphere has a regional character. Because of forcible processes and sedimentation, they are quickly removed from the atmosphere and pollute the underlying surface.

The residence time of aerosol particles in the atmosphere can be estimated through the theory of formation and evolution of aerosol particles in the troposphere, proposed by Rosenberg (1983a,b). According to this theory, the aerosol is considered as a continuously moving or near stationary matter in the process of formation, development and removal from the atmosphere. The so-called ASFV (Aerosol Substance Forming Vapors) are due to the penetration of admixed gases from outside (abundant in the atmosphere). The size of its particles is so small that they neither participate in the energy transformation processes nor influence the atmospheric processes. In the atmosphere, these particles (as several tens of molecules) combine and form clusters, the sizes of which increase subsequently at a cost of the heterogeneous condensation of ASFV and the coagulation growth of the particles. Thus, in the troposphere the so-called macro-dispersion transitional aerosol fraction, with radii between 0.001 and 0.04 μm is formed (some of these particles are destroyed there, due to sticking to larger ones, which are always present in the atmosphere). A special role in the growth of these particles is played by the absorption and desorption of moisture; the radii reach 0.1 μm and their influence on the optical and physical processes in the atmosphere becomes tangible. The subsequent growth of the particles occurs mainly because of the heterogeneous condensation on the surface of aerosol forming substances or their catalytic synthesis. When reaching a radius of more than 1 μm, the aerosol particles go to the sub micron (accumulation) range, which is associated with qualitative change in their properties and behavior.

On the basis of Rosenberg's (1983a,b) theoretical calculations, the residence time of these particles in the troposphere is about 9 days. We tried to check this process experimentally on the eastern coast of the Black Sea in Adjaria (Georgia). For this purpose, after rainy periods during several sunny days, the atmospheric aerosol optical depth was determined by an optical method. The magnitude of this optical depth is mainly dependent on the aerosol particle concentration in the atmosphere. The results show that after a rainy period, the aerosol concentration decreased insignificantly for the first 6-8 hours. Since the second day, a gradual increase in the concentration took place and reached its maximum already been mentioned, redundant humidity – which always characterize the lower atmospheric layers over marine surfaces – leads to an increase of size of the aerosol particles, and thus to an acceleration of the sedimentation. Allowing for this factor, it can be concluded that the residence time of aerosol particles in the atmosphere does not exceed 9-10 days. As a result, it also can be concluded that the active radius of various sources of the tropospheric pollution is confined and has a regional character.

At the present time, there are two methods of air pollution monitoring in the world: the first one consists in air sampling immediately above the earth surface and then determining the concentration and chemical composition of aerosols in laboratories. It is noteworthy that in this method, the natural structure of aerosol particles is destroyed and, as a consequence, the results are estimated as approximate. The other method – so-called non-destructive "actinometric monitoring"- is carried out by means of a remote optical method which determines the relative aerosol concentration within a vertical section of the atmosphere, but does not allow the determination of the aerosol chemical composition.

The objective of this work is to estimate the pollution of the sea surface by atmospheric aerosols in the eastern coastal zone of the Black Sea. For this estimation, data from both the above-mentioned monitoring programmes were used. The aerosols were obtained from observational points located immediately in the coastal zone on the eastern shore of the Black Sea. In the same zone and over the shelf, an optical method was used to determine the pollution of the free atmosphere in a vertical direction.

THE ATMOSPHERIC POLLUTION OVER THE SHELF SURFACE OF THE EASTERN BLACK SEA

The monthly average concentration values for four main pollutants: dust, sulphur dioxide, carbon dioxide and nitrogen dioxide for the period 1981-1990 are given in Table 1. Using these data, the total column densities of the pollutants were calculated in a 10 km atmospheric layer over the sea.

TABLE 1. Monthly average concentrations (mg/m^3) of aerosols over the sea surface in the eastern coastal zone of the Black Sea for the period 1981-1990.

Substance	Months (January – December)											
	1	2	3	4	5	6	7	8	9	10	11	12
Dust	0.2 3	0.1 6	0.1 8	0.2 0	0.2 1	0.1 7	0.2 0	0.2 0	0.2 1	0.1 8	0.1 7	0.1 9
Sulphur dioxide	0.1 4	0.1 2	0.1 1	0.1 0	0.1 2	0.1 1	0.1 2	0.1 0	0.1 6	0.1 6	0.1 1	0.1 5
Carbon dioxide	5.2	3.7	3.7	3.1	4.6	4.7	4.6	3.8	3.7	4.0	3.6	5.0
Nitrogen dioxide	0.0 5	0.0 5	0.0 5	0.0 5	0.0 6	0.0 6	0.0 6	0.0 6	0.0 6	0.0 5	0.0 6	0.0 5

The vertical distributions of the pollutant concentrations in the atmosphere were determined using literature already published. For the vertical distribution of solid particles (dust), the aerosol model of Kondratiev et al. (1983) was used. According to this model, up to 4 km from the surface the concentration is constant, but from 4 km and higher, the concentration decreases exponentially and is well described by (Tavartkiladze, 1989):

$$K_D(z)=K_D(4km)\exp(-[\frac{h}{h_0}]z), \qquad z > 4km \qquad (1)$$

where K_D is the concentration of particles, h the reduced latitude of aerosol particles, h_0 the reduced latitude of the atmosphere and z vertical coordinate. Thus, the total column density of solid particles up to 10 km over the sea surface could be calculated as:

$$K_D=\int_0^4 K_D(0)dz+\int_4^{10} K_D(4)\exp(-[\frac{h}{h_0}]z)dz, \qquad (2)$$

h_0 8 km, while h varies from 1.0 km (winter season) to 1.4 km (summer season) [5]. The results of the calculations for the different months are given in Table 2.

TABLE 2. Total average column density (t/km^2) of aerosols in a 10 km atmospheric layer over the sea surface in the eastern coastal zone of the Black Sea for the period 1

Substance	Months (January - December)											
	1	2	3	4	5	6	7	8	9	10	11	12
Dust	1.5	1.0	1.1	1.2	1.2	1.0	1.2	1.2	1.3	1.1	1.1	1.2
Sulphur	1.1	0.8	0.7	0.6	0.7	0.6	0.6	0.6	0.7	1.1	0.8	1.2
dioxide		7	1	6	4	4	9	1	6		1	
Carbon	52	37	37	31	46	47	46	38	37	40	36	50
dioxide												
Nitrogen	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dioxide	4	3	5	6	6	7	9	7	6	4	6	4

The residence time of sulphur dioxide in the atmosphere is relatively short. It reacts quickly by forming various compounds. The vertical distribution of these compounds in the atmosphere approximates to the distribution of the aerosol optical depth, and the total column density of these compounds could be represented by (Tavartkiladze, 1989):

$$K_{SO2} = \int_0^{10} K_{SO2}(0)\exp(-[\frac{h}{h_0}]z)dz \qquad (3)$$

The total column density of sulphur dioxide in a 10 km layer over the sea surface calculated using (3), is represented in Table 2. It should be noted that these values are underestimated because, as pointed out above, the sulphur dioxide forms various compounds, the mass of which exceeding the mass of SO_2.

The concentration of carbon dioxide in the atmosphere is distributed uniformly according to (Volz et al., 1981):

$$K_{CO} = \int_0^{10} K_{CO2}(0)dz \qquad (4)$$

For the vertical distribution of nitrogen dioxide in the troposphere, a numerical model of Zuev and Komarov (1986) was used. We approximated the proposed model by the exponential law and derived the following expression for the calculation of the total column density in a 10 km layer:

$$K_{NO2} = \int_0^{10} K_{NO2}(0)\exp(-0.35z)dz \qquad (5)$$

Strong seasonal variations of near-earth concentrations of nitrogen oxide are often mentioned in some studies. For example, Noxon (1979) pointed out that the summer near-earth concentration of NO_2 is five times higher than the winter concentrations. According to the data monitoring, no significant seasonal variations have been observed. However, because of the minor amount of NO_2 in the troposphere (the main part is concentrated in the stratosphere), the monitoring data values are, for unknown reasons, underestimated (Zuev and Komarov, (1986). We conjecture that the data on NO_2 in Tables 1 and 2 should be considered as the minimum possible concentration in the atmosphere.

The data represented in Tables 1 and 2 characterize the average of the tropospheric pollution in the eastern part of the Black Sea for the period 1980-1990. Unfortunately, due to a considerable margin of error the data, it was impossible to detect the dynamics of the air pollution in time. The possibility of determination of this dynamics and sorting out of background, anthropogenic and random factors of the atmospheric pollution is provided by the "actinometric monitoring", or remote optical methods.

Figure 1 represents the variations of annual mean values of the atmospheric aerosol optical depth calculated through methods described by Tavartkiladze (1989) which, practically without any ambiguity, determine the total content of aerosol particles in a vertical column of the atmosphere. The curve 1 in Figure 1 determines the level of background pollution always present in the atmosphere; its annual mean values are rather uniform. Curve 2 gives the level of background + anthropogenic pollution and curve 3 represents the total level (background + anthropogenic + random) of atmospheric pollution.

Random sources could be both of natural (strong volcanic eruptions, forest fires, etc.) and anthropogenic (near-surface atomic explosions, industrial emergencies, etc.) origin. For example, as shown in Figure 1, the maximum level of air pollution in the eastern part of the Black Sea was observed in 1983. It was caused by the eruption of volcano "El-Chichón" in Mexico, in February 1982. In order to track the air pollution by random sources in more detail, the monthly air pollution variations from January 1980 to December 1990 are represented in Figure 2. In view to exclude the intra-annual variations, the curve is plotted in relative pollution units (the ratio of the actual optical depth to the monthly average during 1980-1990). As shown in Figure 2 the volcanic material reached the eastern coast of the Black Sea in 5-6 months and the subsequent gradual purification of the atmosphere took almost two years.

In contrast to the random sources, the anthropogenic pollution shows a gradual systematic increase over the eastern part of the Black Sea, beginning from 1940. It reaches a maximum in 1984-1986, displaying a slight decrease after this period. In order to compare the data in Table 1 and 2 with the data of "actinometric monitoring", the mean values of the background, anthropogenic and total pollution for the period 1980-1990 have been computed. The averages of the background, anthropogenic and the mean optical depth of the random sources of aerosol levels are 0.021, 0.064 and 0.042 t/km^2 respectively, representing 16.5%, 50.4% and 33.1% of the total pollution. Thus, the total mean optical depth of aerosol level reaches 0.127 t/km^2 at a wavelength of 1μm.

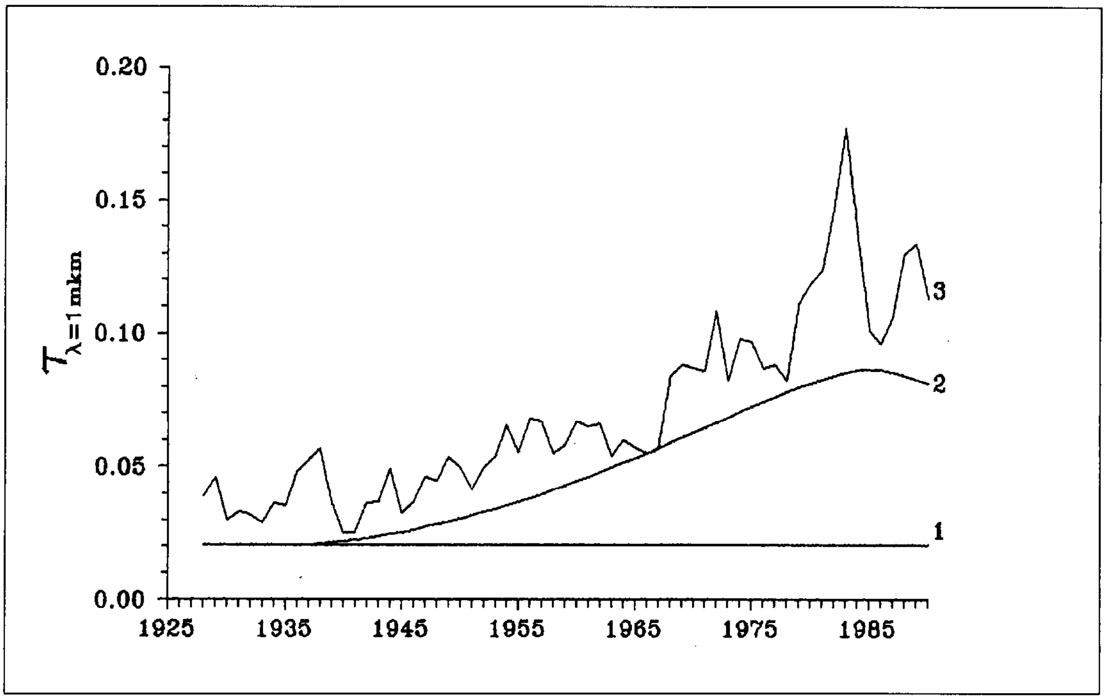

FIGURE 1. Variation of the background (curve 1), background +anthropogenic (curve 2) and total pollution (curve 3) of the atmosphere over the eastern part of the Black Sea in the period 1928 - 1990.

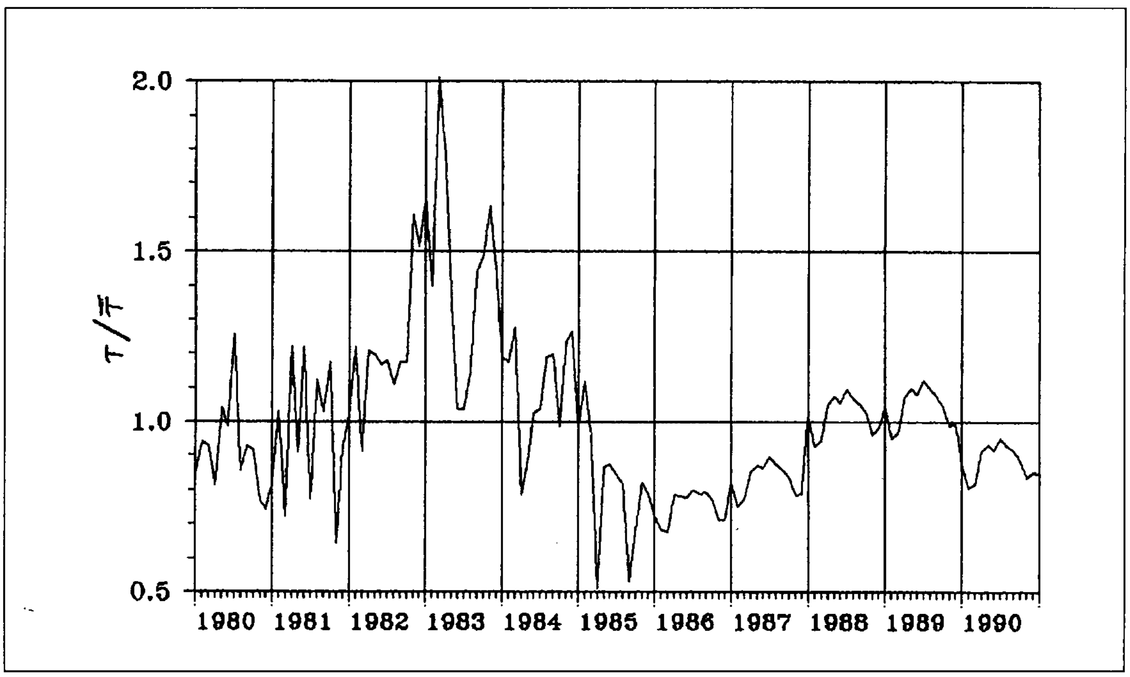

FIGURE 2. Relative variation of the monthly mean total pollution of the atmosphere over the eastern part of the Black Sea in the period January 1980 - December 1990.

POLLUTION OF THE SEA SURFACE BY ATMOSPHERIC AEROSOLS

As previously mentioned, the average life time of aerosol particles in the troposphere is 5 to 6 days if forcible atmospheric processes, such as precipitation, do not blow them prematurely away from the atmosphere. To carry out an approximate assessment of the increase of aerosol mass after precipitation, the results of the above-mentioned experiment have been used to determine the optical depth variations after raining, when forcible processes removing aerosols from the atmosphere are not presented. The variation of the optical depth after a rainy period ($\Delta\tau/\tau$) could be represented as follows:

$$\frac{\Delta\tau}{\tau} = \begin{cases} 0 & n \leq 1.6 \text{ days} \\ 0.018\,n - 0.03 & 1.6 < n \leq 6 \text{ days} \\ 0.067 & n > 6 \text{ days} \end{cases} \qquad (6)$$

where n is the number of days after the precipitation. Tavartkiladze (1989) showed that during 1.6 days (approximately 38 hours) after the precipitation, the aerosol optical depth does not change. After this time, a linear increase up to the sixth day of precipitation is observed, and then the increase ceases.

Considering these results, we present the following model of atmospheric purification in which the removal of aerosol particles from the troposphere starts 38 hours after the precipitation. If during the subsequent 6 days there is no precipitation, the aerosol mass in the atmosphere increases by about 7%. The precipitation removes from the troposphere the quantity of aerosol particles generated after the previous precipitation. If precipitation does not occur after more than 6 days, then the normal sedimentation through the atmosphere acts as a means of precipitation, removing about 7% of the total aerosol mass sediments from the troposphere. Thus, in order to determine the quantity of aerosols deposited in sediment on to the underlying surface, it is necessary to know the total mass of aerosol particles in a vertical air column of troposphere with a cross-section unit, the number of precipitation events per time unit (month, year) and the period (hours, days) between the precipitation events.

In order to calculate the quantity of aerosol sediments in the proposed model, one should calculate also the minimum quantity of precipitation, which limits the process of the aerosol removal. It is known that the scavenging ends mainly at the initial stage of precipitation. At present, it is unclear what quantity of precipitation limits the removal. Thus, calculations have been performed, taking into consideration the number of days with precipitation (q) >1 mm, >5 mm and > 10 mm. It is proposed that the removal process be finished namely in this range.

Table 3 represents the mean monthly duration of precipitation in hours; the mean number of days with precipitation $q > 1$ mm, $q > 5$ mm and $q > 10$ mm; and the mean duration of the period without precipitation for the eastern part of the Black Sea. This table is also showing the computed average quantities of pollutants (in t/km^2) deposited on to the sea surface from the atmosphere (more correctly from the troposphere) in the eastern part of the Black Sea during 1980-1990. The calculation of the dynamics of deposited admixtures does not represent any problem if the annual variation of the aerosol optical depth is known (Figure 1).

TABLE 3. Number of precipitation events; quantity of atmospheric pollutants in t/km^2 deposited on to the sea surface in the eastern part of the Black Sea

Months	1	2	3	4	5	6	7	8	9	10	11	12	Total
Duration (hours)	174	165	176	121	82	69	71	81	106	120	131	155	1451
Precipitation (q)													
q>1 mm	14	13	13	10	8	10	11	11	12	11	12	13	138
q>5 mm	11	10	9	6	4	6	7	7	9	9	9	10	97
q>10 mm	8	7	6	4	2	4	4	6	7	7	7	8	70
Duration without precipitation (days)	1.7	1.6	1.8	2.5	3.4	2.7	2.5	2.1	2.5	2.4	2.0	1.9	
q>1 mm	0.01	0.00	0.04	0.18	0.32	0.19	0.20	0.20	0.13	0.15	0.09	0.06	1.58
Dust q>5 mm	0.01	0.00	0.02	0.11	0.16	0.11	0.13	0.13	0.10	0.13	0.06	0.05	1.01
q>10 mm	0.01	0.00	0.02	0.07	0.08	0.07	0.07	0.11	0.08	0.10	0.05	0.04	0.70
q> 1 mm	0.01	0.00	0.03	0.10	0.19	0.12	0.12	0.10	0.08	0.15	0.07	0.06	1.02
SO_2 q> 5 mm	0.01	0.00	0.02	0.06	0.10	0.07	0.08	0.06	0.06	0.12	0.05	0.05	0.67
q> 10 mm	0.00	0.00	0.01	0.04	0.05	0.05	0.04	0.06	0.04	0.09	0.04	0.04	0.47
q>1 mm	0.4	0.0	1.3	4.6	11.8	8.8	8.0	6.4	3.7	5.5	2.9	2.6	56.2
CO_2 q>5 mm	0.3	0.0	0.9	2.8	5.9	5.3	5.1	4.0	2.8	4.5	2.2	2.0	35.9
q>10 mm	0.2	0.0	0.6	1.9	2.9	3.5	2.9	3.5	2.2	3.5	1.7	1.6	24.6
q>1 mm	0.00	0.00	0.01	0.02	0.04	0.03	0.03	0.03	0.02	0.02	0.01	0.01	0.22
NO_2 q>5 mm	0.00	0.00	0.00	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.14
q>10 mm	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.00	0.10

CONCLUSIONS

The atmospheric inputs are important for the pollution of the Black Sea. The background level of the atmospheric pollution does not contribute significantly to the pollution of the Black Sea. Random factors of strong atmospheric pollution (volcanic eruptions, forest fires, etc.) periodically pollute the water surface. They can cause only short-term (maximum of several years) variations in the amount of particles depositing on the sea surface, but do not take part in the tendency to pollute the sea.

The increasing anthropogenic pollution of the atmosphere has been contributing significantly to the pollution of the eastern Black Sea since 1940. This has caused an increase in the amount of aerosol particles delivered to the sea. After 1984-1986, a small decrease in the anthropogenic pollution of the atmosphere over the eastern part of the Black Sea has been observed.

The total density of the column of dust, sulphur dioxide, carbon dioxide and nitrogen dioxide within a 10 km layer over the sea surface has been calculated using the data of the monitoring programme on near-earth air quality. A model of removal of polluting components from the troposphere via precipitation and sedimentation was proposed, and the possible minimum and maximum quantities of these substances were calculated. It is estimated that during the period 1980-1990, the eastern part of the Black Sea has received, per km^2, an annual average of 0.7-1.58 t of solid aerosols (dust); 0.47-1.02 t of sulphur compounds; 0.1 - 0.22 t of nitrogen dioxide; and 14.6-56.2 t of carbon dioxide.

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GIS FOR REGIONAL SEAS PROGRAMMES. A CASE STUDY: THE BLACK SEA

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INTRODUCTION

The Black Sea: A Unique Environment in Crisis

Almost one third of the land area of continental Europe drains into the Black Sea. This area includes major parts of seventeen countries, thirteen capitals and some 160 million persons. The second, third and fourth most important European rivers discharge into this sea, but its only connection to the world's oceans is the narrow Bosphorus Channel. The Bosphorus is around 70 meters deep and 700 meters wide, but the depth of the Black Sea itself exceeds two kilometers in some places. The Black Sea is the biggest natural anoxic basin in the world. Despite this situation, for millennia its surface waters supported a rich and diverse marine life. The inhabitants of the coastal zone have also benefited from the advantages of abundant fisheries and, more recently, from the millions of tourists who flocked from all the eastern and central Europe countries to bathe in its warm waters and enjoy the beauty of its shorelines, plains and mountains.

In a period of only three decades, the Black Sea has suffered the catastrophic degradation of a major part of its natural resources. Increased loads of nutrients from rivers caused an overproduction of tiny phytoplankton which, in turn, prevented the light to reach the sea grasses and algae, essential components of the sensitive ecosystem of the northwestern shelf. The entire ecosystem began to collapse. This problem, coupled with pollution and irrational exploitation of fish stocks, started a sharp decline in fisheries resources. A poor planning has destroyed much of the aesthetic resources of the coastline. The uncontrolled pollution caused by sewage resulted in frequent beach closures and considerable financial losses for the tourist industry. In some places, the solid waste is being dumped directly in the sea or on valuable wetlands. Tanker accidents and operational discharges have often caused oil pollution. These problems have reached a crisis level at a time when five of the Black Sea countries are facing an economic and social transition and experiment difficulties to take the necessary urgent measures to solve them.

In order to make an early start to an environmental action and to develop a longer-term Action Plan, the Black Sea countries requested support from the Global Environment Facility (GEF), a fund established in 1991 under the management of the World Bank, the UN Development Programme and the UN Environmental Programme. In June 1993, a three-year Black Sea Environmental Programme was established.

THE BLACK SEA ENVIRONMENTAL PROGRAMME

The GEF Black Sea Environmental Programme has three primary objectives:

(i) To strengthen and create regional capacities for managing the Black Sea ecosystem;
(ii) To develop and implement an appropriate policy and legal framework for the assessment, control and prevention of pollution and the maintenance and enhancement of biodiversity;
(iii) To facilitate the preparation of sound environmental investments.

The BSEP is being implemented through an interactive matrix of national co-ordinators, thematic regional activity centres and focal point institutions whose targets are: emergency response, routine pollution monitoring, special monitoring, biodiversity protection, coastal zone management, environmental legislation and economics, data management and GIS, and fisheries. A Project Co-ordination (PCU) based in Istanbul, conducts the overall programme co-ordination.

The Working Party on Data Management and GIS (GISWP) was established in 1993 by the PCU in order to ensure a region-wide compatibility in the generation and management of databases, and promote data exchange. The Working Party includes at least an expert (Contact Person) from every country of the Black Sea, together with additional external expertise where appropriate. The Working Party pays particular attention to the Geographical Information System as a mean to communicate data to environmental managers, decision-makers and the general public.

It was agreed that all existing *maps,* which will be collected by the GISWP, should be digitized in the Moscow State University (MSU), Department of Cartography and Geoinformatics. The MSU was also responsible for the distribution of special GIS software to the participants in the project, as well as for the organization of the relevant training workshops.

The data have been digitized in their institute of origin and transferred to MSU. In close association with the PCU and selected experts, the MSU staff was responsible for the accumulation and transformation of all data into a GIS, and the development of a user interface for the system. They were also responsible for the development of a modelling system for the creation of digital models of the GIS layers, development of the DBMS "Black Sea" thematic query as well as for development of the DBMS "Black Sea" geometric query.

Data quality assurance is an essential element in the success of the GIS strategy. Data gathered for incorporation in the GIS DATABASE should be accompanied by full information, which will enable evaluation of their quality. This should include information on methodologies employed, inter-comparison exercises (where relevant) and estimated uncertainties.

The Black Sea Geographic Information System has been developed for use by governments, scientists, the general public, NGO's and the media for the following purposes:

- Planning for marine environmental activities and impacts on a regional scale;
- Public awareness through training, education, workshops, lectures, and media;
- Scientific analysis, modelling ecological impact assessment, science planning.

The main GIS components are designed to perform the following functions:

- Data input;
- Data storage and database management;
- Data analysis and processing;
- Interaction with the user (graphics/map editing); and
- Data output and presentation (plotting)

THE BLACK SEA GIS

The development of GIS involved two major activities:

o Development of a special software package for: (i) digitizing, editing and storing cartographic information; (ii) modelling of continual geofields; (iii) processing of digital models and creation of thematic maps; (iv) transformation of geographic co-ordinate into planner co-ordinates of

Mercator projection and; (v) finally, for demonstration of data. This task was the responsibility of the Department of Cartography and Geoinformatics of the Moscow State University.

- Collection of basic historical data on the Black Sea, processing and integration of data already in the system, as well as collection and processing of new data produced by the different thematic Working Parties of the BSEP.

The system consists of seven thematic blocks representing different sides of the Black Sea ecosystem. In each block, there is a set of map layers describing different aspects of the Black Sea ecosystem functioning. A relational database is available for some maps.

In order to better understand and manage the ecological and anthropogenic processes, it is necessary to understand the physical process forming the base of the Black Sea ecosystem; the composition of the landscape and human distribution, as well as many other important processes, which constitute the unique environment of the Black Sea.

Geography

General cartographic information on the Black Sea is presented in this block. The map of the Black Sea drainage basin represents almost one third of the land area of continental Europe. This area includes major parts of seventeen countries, thirteen capitals and some 160 million persons. The second, third and fourth most important European rivers discharge into this sea. The information on water and sediment discharges of all Black Sea rivers is available in the system. The Political map of the Black Sea area shows the countries at the same scale and methodology. In some countries, regional maps from municipalities and administrations are accessible.

Geology

This block provides a general picture of the geological processes in the Black Sea including maps on the geological evolution of the Black Sea basin; map of Historical hazards in the BS region; Tectonic sketch of the Black sea; Geological cross-section across the Black Sea; Tectonic sketch of the Black Sea region; map of Bottom sediments of the Black Sea; and map of Geomorphologic classification of the Black Sea coastline with major coastal sediment drift and coastal erosion. The evolution of the Danube Delta during the Holocene and the relative sea level rise data, obtained from 48 stations around the Black Sea, constitute a very important part of this block, covering an observation period of a hundred years.

Meteorology

The most important meteorological parameters describing typical conditions in the Black Sea region are presented, using animation possibility of the system. This monthly average data were extracted from data archives of the Hydrometeorological Service of the former Soviet Union. They are giving general information on air temperature, precipitation, evaporation, cloudiness, wind processes, sunny and rainy days, and other main elements of ice regime in the NW shelf.

Physical Oceanography

Physical processes occurring in the sea are playing a very important role in the formation of water masses of the sea, as well as regards specific hydrological regime in the marine ecosystem. The oceanography of the Black Sea was very well studied during the last century. Many scientific hydrological regimes in the ecosystem of oceanography of the Black Sea have been very well studied during the last century. Many scientific cruises (map of oceanographic station network in the Black Sea) collected thousands of data records on most important parameters. Based on this data, a set of maps showing the climatic oceanography of the Black Sea (temperature and salinity for each month and each season for 20 standard depths) as well as major water masses of the Black Sea have been incorporated in the system.

Recent international programmes in the Black sea have also taken into account the scientific interdisciplinary studies, with the main objective to collect physical and chemical data using the common methodology, instruments, intercalibration and strict quality control. The most reliable data have been collected during CoMSBlack surveys in 1992 and 1993. These data were used in the preparation of a set of maps showing the distribution of temperature, salinity, dynamic topography, density anomaly, and Cold intermediate layer in the Black Sea, for 11 standard depths. The Secci disk depth climatic maps have been prepared on the basis of CoMSBlack data. The map of seasonal mean circulation describes the general tendency of the horizontal movements of the Black Sea waters. The system is also supplied by satellite data on the sea surface temperature originated by theNOAA.

Chemical Oceanography and Pollution

Data set generated during CoMSBlack 1992 and 1993 have been used for the preparation of the maps showing the spatial distribution of the following parameters in the Black Sea for 11 standard depth: dissolved oxygen, hydrogen sulphide, inorganic nitrogen, inorganic phosphates and silicic acid.

In 1995, the Black Sea Environmental Programme organized a survey of the Land-based sources of pollution in all 6 Black Sea countries, using the standard WHO methodology. The data collected during this survey are included in the system. The results of the sediment pollution survey carried out in 1995 in the open sea (Polygons study) are reported on the map representing the state of the Black Sea pollution.

The location of the upper boundary of the hydrogen sulphide zone for different years and areas of hypoxia are shown on the relevant maps. Specific information on the oil products and heavy metals pollution in the northwestern Black Sea shelf is also available in the system.

Biology

The main objective of this block is to demonstrate the richness of the Black Sea ecosystem in terms of biological diversity, present key species habitats, important protected areas as well as to illustrate the problems faced by the Black Sea ecosystem. The map showing the distribution of wetlands around the Black Sea gives detailed information on each of them. The system includes maps of existing natural reserves, sensitive species habitats, distribution of some exotic species of phytoplankton, zooplankton and macrozoobenthos which demonstrate the biological productivity of the Black Sea waters. A Vegetation index and Chlorophyll A distribution maps generated on the basis of CZCS data; maps on the decrease of sea grass meadows on the Black Sea shelf; as well as maps on accidental and intentional introduction of species in the Back Sea conclude the biology block.

Fisheries

Based on data archival on fishery research activities of the Soviet Union in the Black Sea during 1980-1991, a set of digital maps was prepared, showing the spatial distribution of two commercial species (anchovy and sprat) in the Black Sea. The following layers have been prepared: spawning stock distribution, eggs and larvae distribution.

Maps of distribution and migration of turbot, whiting, sturgeon, sprat, shad, red mullet, thornback ray, mullet, Mediterranean horse mackerel, mackerel, picked dogfish, bluefish, Atlantic bonito, anchovy in the Black Sea have been prepared using FAO publications.

CONCLUSIONS

We have presented a recently developed GIS covering the large-scale region of the Black Sea. This system has been created using exiting and recently obtained data which constitute a wide range of national and international data sources. Eleven scientific institutions and more than 50 experts have contributed to the development of the Black Sea GIS. We recognize that the quality of the data and its resolution varies between countries and according to the different topics. Still this GIS is, as far as we know, the first multidisciplinary and comprehensive study in the Black Sea region, we do hope that it will be useful for scientists and managers, for all friends of the Black Sea and all those who want to protect and save it.

IOC Workshop Reports

The Scientific Workshops of the Intergovernmental Oceanographic Commission are sometimes jointly sponsored with other intergovermental or non-governmental bodies. In most cases, IOC assumes responsibility for printing, and copies may be requested from:

Intergovernmental Oceanographic Commission - UNESCO
1, rue Miollis, 75732 Paris Cedex 15, France

No.	Title	Languages
1	CCOP-IOC, 1974, Metallogenesis, Hydrocarbons and Tectonic Patterns in Eastern Asia (Report of the IDOE Workshop on); Bangkok, Thailand, 24-29 September 1973 UNDP (CCOP), 138 pp.	E (out of stock)
2	CICAR Ichthyoplankton Workshop, Mexico City, 16-27 July 1974 (UNESCO Technical Paper in Marine Sciences, No. 20).	E (out of stock) S (out of stock)
3	Report of the IOC/GFCM/ICSEM International Workshop on Marine Pollution in the Mediterranean; Monte Carlo, 9-14 September 1974.	E, F E (out of stock)
4	Report of the Workshop on the Phenomenon known as 'El Niño'; Guayaquil, Ecuador, 4-12 December 1974.	E (out of stock) S (out of stock)
5	IDOE International Workshop on Marine Geology and Geophysics of the Caribbean Region and its Resources; Kingston, Jamaica, 17-22 February 1975.	E (out of stock) S
6	Report of the CCOP/SOPAC-IOC IDOE International Workshop on Geology, Mineral Resources and Geophysics of the South Pacific; Suva, Fiji, 1-6 September 1975.	E
7	Report of the Scientific Workshop to Initiate Planning for a Co-operative Investigation in the North and Central Western Indian Ocean, organized within the IDOE under the sponsorship of IOC/FAO (IOFC)/UNESCO/EAC; Nairobi, Kenya, 25 March-2 April 1976.	E, F, S, R
8	Joint IOC/FAO (IPFC)/UNEP International Workshop on Marine Pollution in East Asian Waters; Penang, 7-13 April 1976.	E (out of stock)
9	IOC/CMG/SCOR Second International Workshop on Marine Geoscience; Mauritius, 9-13 August 1976.	E, F, S, R
10	IOC/WMO Second Workshop on Marine Pollution (Petroleum) Monitoring; Monaco, 14-18 June 1976.	E, F E (out of stock) R
11	Report of the IOC/FAO/UNEP International Workshop on Marine Pollution in the Caribbean and Adjacent Regions; Port of Spain, Trinidad, 13-17 December 1976.	E, S (out of stock)
11 Suppl.	Collected contributions of invited lecturers and authors to the IOC/FAO/UNEP International Workshop on Marine Pollution in the Caribbean and Adjacent Regions; Port of Spain, Trinidad, 13-17 December 1976.	E (out of stock), S
12	Report of the IOCARIBE Interdisciplinary Workshop on Scientific Programmes in Support of Fisheries Projects; Fort-de-France, Martinique, 28 November-2 December 1977.	E, F, S
13	Report of the IOCARIBE Workshop on Environmental Geology of the Caribbean Coastal Area; Port of Spain, Trinidad, 16-18 January 1978.	E, S
14	IOC/FAO/WHO/UNEP International Workshop on Marine Pollution in the Gulf of Guinea and Adjacent Areas; Abidjan, Côte d'Ivoire, 2-9 May 1978.	E, F
15	CPPS/FAO/IOC/UNEP International Workshop on Marine Pollution in the South-East Pacific; Santiago de Chile, 6-10 November 1978.	E (out of stock)
16	Workshop on the Western Pacific, Tokyo, 19-20 February 1979.	E, F, R
17	Joint IOC/WMO Workshop on Oceanographic Products and the IGOSS Data Processing and Services System (IDPSS); Moscow, 9-11 April 1979.	E
17 Suppl.	Papers submitted to the Joint IOC/WMO Seminar on Oceanographic Products and the IGOSS Data Processing and Services System; Moscow, 2-6 April 1979.	E
18	IOC/UNESCO Workshop on Syllabus for Training Marine Technicians; Miami, U.S.A., 22-26 May 1978 (UNESCO reports in marine sciences, No. 4 published by the Division of Marine Sciences, UNESCO).	E (out of stock), F, S (out of stock), R
19	IOC Workshop on Marine Science Syllabus for Secondary Schools; Llantwit Major, Wales, U.K., 5-9 June 1978 (UNESCO reports in marine sciences, No. 5, published by the Division of Marine Sciences, UNESCO).	E (out of stock), E, S, R, Ar
20	Second CCOP-IOC Workshop on IDOE Studies of East Asia Tectonics and Resources; Bandung, Indonesia, 17-21 October 1978.	E
21	Second IDOE Symposium on Turbulence in the Ocean; Liège, Belgium, 7-18 May 1979.	E, F, S, R
22	Third IOC/WMO Workshop on Marine Pollution Monitoring; New Delhi, 11-15 February 1980.	E, F, S, R
23	WESTPAC Workshop on the Marine Geology and Geophysics of the North-West Pacific; Tokyo, 27-31 March 1980.	E, R
24	WESTPAC Workshop on Coastal Transport of Pollutants; Tokyo, Japan, 27-31 March 1980.	E (out of stock)
25	Workshop on the Intercalibration of Sampling Procedures of the IOC/ WMO UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open-Ocean Waters; Bermuda, 11-26 January 1980.	E (superseded by IOC Technical Series No. 22)
26	IOC Workshop on Coastal Area Management in the Caribbean Region; Mexico City, 24 September-5 October 1979.	E, S
27	CCOP/SOPAC-IOC Second International Workshop on Geology, Mineral Resources and Geophysics of the South Pacific; Nouméa, New Caledonia, 9-15 October 1980.	E
28	FAO/IOC Workshop on the effects of environmental variation on the survival of larval pelagic fishes. Lima, 20 April-5 May 1980.	E
29	WESTPAC Workshop on Marine Biological Methodology; Tokyo, 9-14 February 1981.	E
30	International Workshop on Marine Pollution in the South-West Atlantic; Montevideo, 10-14 November 1980.	E (out of stock) S
31	Third International Workshop on Marine Geoscience; Heidelberg, 19-24 July 1982.	E, F, S
32	UNU/IOC/UNESCO Workshop on International Co-operation in the Development of Marine Science and the Transfer of Technology in the context of the New Ocean Regime; Paris, France, 27 September-1 October 1982.	E, F, S
32 Suppl.	Papers submitted to the UNU/IOC/UNESCO Workshop on International Co-operation in the Development of Marine Science and the Transfer of Technology in the Context of the New Ocean Regime; Paris, France, 27 September-1 October 1982.	E
33	Workshop on the IREP Component of the IOC Programme on Ocean Science in Relation to Living Resources (OSLR); Halifax, 26-30 September 1963.	E
34	IOC Workshop on Regional Co-operation in Marine Science in the Central Eastern Atlantic (Western Africa); Tenerife, 12-17 December 1963.	E, F, S
35	CCOP/SOPAC-IOC-UNU Workshop on Basic Geo-scientific Marine Research Required for Assessment of Minerals and Hydrocarbons in the South Pacific; Suva, Fiji, 3-7 October 1983.	E
36	IOC/FAO Workshop on the Improved Uses of Research Vessels; Lisbon, Portugal, 28 May-2 June 1984.	E
36 Suppl.	Papers submitted to the IOC/FAO Workshop on the Improved Uses of Research Vessels; Lisbon, Portugal, 28 May-2 June 1984.	E
37	IOC/UNESCO Workshop on Regional Co-operation in Marine Science in the Central Indian Ocean and Adjacent Seas and Gulfs; Colombo, 8-13 July 1985.	E
38	IOC/ROPME/UNEP Symposium on Fate and Fluxes of Oil Pollutants in the Kuwait Action Plan Region; Basrah, Iraq, 8-12 January 1984.	E
39	CCOP (SOPAC)-IOC-IFREMER-ORSTOM Workshop on the Uses of Submersibles and Remotely Operated Vehicles in the South Pacific; Suva, Fiji, 24-29 September 1985.	E
40	IOC Workshop on the Technical Aspects of Tsunami Analysis, Prediction and Communications; Sidney, B.C., Canada, 29-31 July 1985.	E
40 Suppl.	First International Tsunami Workshop on Tsunami Analysis, Prediction and Communications, *Submitted Papers;* Sidney, B.C., Canada, 29 July - 1 August 1985.	E
41	First Workshop of Participants in the Joint FAO/IOC/WHO/IAEA/UNEP Project on Monitoring of Pollution in the Marine Environment of the West and Central African Region (WACAF/2); Dakar, Senegal, 28 October-1 November 1985.	E
43	IOC Workshop on the Results of MEDALPEX and Future Oceanographic Programmes in the Western Mediterranean; Venice, Italy, 23-25 October 1985.	E
44	IOC-FAO Workshop on Recruitment in Tropical Coastal Demersal Communities; Ciudad del Carmen, Campeche, Mexico, 21-25 April 1986.	E (out of stock) S
44 Suppl.	IOC-FAO Workshop on Recruitment in Tropical Coastal Demersal Communities, *Submitted Papers;* Ciudad del Carmen, Campeche, Mexico, 21-25 April 1986.	E
45	IOCARIBE Workshop on Physical Oceanography and Climate; Cartagena, Colombia, 19-22 August 1986.	E
46	Reunión de Trabajo para Desarrollo del Programa "Ciencia Oceánica en Relación a los Recursos No Vivos en la Región del Atlántico Sud-occidental"; Porto Alegre, Brazil, 7-11 de abril de 1986.	S
47	IOC Symposium on Marine Science in the Western Pacific: The Indo-Pacific Convergence; Townsville, 1-6 December 1966.	E
48	IOCARIBE Mini-Symposium for the Regional Development of the IOC-UN (OETB) Programme on 'Ocean Science in Relation to Non-Living Resources (OSNLR)'; Havana, Cuba, 4-7 December 1986.	E, S
49	AGU-IOC-WMO-CPPS Chapman Conference: An International Symposium on 'El Niño'; Guayaquil, Ecuador, 27-31 October 1986.	E
50	CCALR-IOC Scientific Seminar on Antarctic Ocean Variability and its Influence on Marine Living Resources, particularly Krill (organized in collaboration with SCAR and SCOR); Paris, France, 2-6 June 1987.	E
51	CCOP/SOPAC-IOC Workshop on Coastal Processes in the South Pacific Island Nations; Lae, Papua-New Guinea, 1-8 October 1987.	E

No.	Title	Languages
52	SCOR-IOC-UNESCO Symposium on Vertical Motion in the Equatorial Upper Ocean and its Effects upon Living Resources and the Atmosphere; Paris, France, 6-10 May 1985.	E
53	IOC Workshop on the Biological Effects of Pollutants; Oslo, 11-29 August 1986.	E
54	Workshop on Sea-Level Measurements in Hostile Conditions; Bidston, UK, 28-31 March 1988	E
55	IBCCA Workshop on Data Sources and Compilation, Boulder, Colorado, 18-19 July 1988.	E
56	IOC-FAO Workshop on Recruitment of Penaeid Prawns in the Indo-West Pacific Region (PREP); Cleveland, Australia, 24-30 July 1988.	E
57	IOC Workshop on International Co-operation in the Study of Red Tides and Ocean Blooms; Takamatsu, Japan, 16-17 November 1987.	E
58	International Workshop on the Technical Aspects of the Tsunami Warning System; Novosibirsk, USSR, 4-5 August 1989.	E
58 Suppl.	Second International Workshop on the Technical Aspects of Tsunami Warning Systems, Tsunami Analysis, Preparedness, Observation and Instrumentation. *Submitted Papers*; Novosibirsk, USSR, 4-5 August 1989.	E
59	IOC-UNEP Regional Workshop to Review Priorities for Marine Pollution Monitoring Research, Control and Abatement in the Wider Caribbean; San José, Costa Rica, 24-30 August 1989.	E, F, S
60	IOC Workshop to Define IOCARIBE-TRODERP proposals; Caracas, Venezuela, 12-16 September 1989.	E
61	Second IOC Workshop on the Biological Effects of Pollutants; Bermuda, 10 September-2 October 1988.	E
62	Second Workshop of Participants in the Joint FAO-IOC-WHO-IAEA-UNEP Project on Monitoring of Pollution in the Marine Environment of the West and Central African Region; Accra, Ghana, 13-17 June 1988.	E
63	IOC/WESTPAC Workshop on Co-operative Study of the Continental Shelf Circulation in the Western Pacific; Bangkok, Thailand, 31 October-3 November 1989.	E
64	Second IOC-FAO Workshop on Recruitment of Penaeid Prawns in the Indo-West Pacific Region (PREP); Phuket, Thailand, 25-31 September 1989.	E
65	Second IOC Workshop on Sardine/Anchovy Recruitment Project (SARP) int he Southwest Atlantic; Montevideo, Uruguay, 21-23 August 1989.	E
66	IOC *ad hoc* Expert Consultation on Sardine/Anchovy Recruitment Programme; La Jolla, California, U.S.A., 1989.	E
67	Interdisciplinary Seminar on Research Problems in the IOCARIBE Region; Caracas, Venezuela, 28 November-1 December 1989.	E (out of stock)
68	International Workshop on Marine Acoustics; Beijing, China, 26-30 March 1990.	E
69	IOC-SCAR Workshop on Sea-Level Measurements in the Antarctica; Leningrad, USSR, 28-31 May 1990.	E
69 Suppl.	IOC-SCAR Workshop on Sea-Level Measurements in the Antarctica; *Submitted Papers*; Leningrad, USSR, 28-31 May 1990.	E
70	IOC-SAREC-UNEP-FAO-IAEA-WHO Workshop on Regional Aspects of Marine Pollution; Mauritius, 29 October - 9 November 1990.	E
71	IOC-FAO Workshop on the Identification of Penaeid Prawn Larvae and Postlarvae; Cleveland, Australia, 23-28 September 1990.	E
72	IOC/WESTPAC Scientific Steering Group Meeting on Co-Operative Study of the Continental Shelf Circulation in the Western Pacific; Kuala Lumpur; Malaysia, 9-11 October 1990.	E
73	Expert Consultation for the IOC Programme on Coastal Ocean Advanced Science and Technology Study; Liège, Belgium, 11-13 May 1991.	E
74	IOC-UNEP Review Meeting on Oceanographic Processes of Transport and Distribution of Pollutants in the Sea; Zagreb, Yugoslavia, 15-18 May 1989.	E
75	IOC-SCOR Workshop on Global Ocean Ecosystem Dynamics; Solomons, Maryland, U.S.A., 29 April-2 May 1991.	E
76	IOC/WESTPAC Scientific Symposium on Marine Science and Management of Marine Areas of the Western Pacific; Penang, Malaysia, 2-6 December 1991.	E
77	IOC-SAREC-KMFRI Regional Workshop on Causes and Consequences of Sea-Level Changes on the Western Indian Ocean Coasts and Islands; Mombasa, Kenya, 24-28 June 1991.	E
78	IOC-CEC-ICES-WMO-ICSU Ocean Climate Data Workshop Goddard Space Flight Center; Greenbelt, Maryland, U.S.A., 18-21 February 1992.	E
79	IOC/WESTPAC Workshop on River Inputs of Nutrients to the Marine Environment in the WESTPAC Region; Penang, Malaysia, 26-29 November 1991.	E
80	IOC-SCOR Workshop on Programme Development for Harmful Algae Blooms; Newport, U.S.A., 2-3 November 1991.	E
81	Joint IAPSO-IOC Workshop on Sea Level Measurements and Quality Control; Paris, France, 12-13 October 1992.	E
82	BORDOMER 92: International Convention on Rational Use of Coastal Zones. A Preparatory Meeting for the Organization of an International Conference on Coastal Change; Bordeaux, France, 30 September-2 October 1992.	E
83	IOC Workshop on Donor Collaboration in the Development of Marine Scientific Research Capabilities in the Western Indian Ocean Region; Brussels, Belgium, 12-13 October 1992.	E
84	Workshop on Atlantic Ocean Climate Variability; Moscow, Russian Federation, 13-17 July 1992.	E
85	IOC Workshop on Coastal Oceanography in Relation to Integrated Coastal Zone Management; Kona, Hawaii, 1-5 June 1992.	E
86	International Workshop on the Black Sea; Varna, Bulgaria 30 September - 4 October 1991.	E
87	Taller de trabajo sobre efectos biológicos del fenómeno «El Niño» en ecosistemas costeros del Pacífico Sudeste; Santa Cruz, Galápagos, Ecuador, 5-14 de octubre de 1989.	S only (Summary in E, F, S)
88	IOC-CEC-ICSU-ICES Regional Workshop for Member States of Eastern and Northern Europe (GODAR Project); Obninsk, Russia, 17-20 May 1993.	E
89	IOC-ICSEM Workshop on Ocean Sciences in Non-Living Resources; Perpignan, France, 15-20 October 1990.	E
90	IOC Seminar on Integrated Coastal Management; New Orleans, U.S.A., 17-18 July 1993.	E
91	Hydroblack'91 CTD Intercalibration Workshop; Woods Hole, U.S.A., 1-10 December 1991.	E
92	Réunion de travail IOCEA-OSNLR sur le Projet « Budgets sédimentaires le long de la côte occidentale d'Afrique » Abidjan, Côte d'Ivoire, 26-28 juin 1991.	F
93	IOC-UNEP Workshop on Impacts of Sea-Level Rise due to Global Warming. Dhaka, Bangladesh, 16-19 November 1992.	E
94	BMTC-IOC-POLARMAR International Workshop on Training Requirements in the Field of Eutrophication in Semi-Enclosed Seas and Harmful Algal Blooms, Bremerhaven, Germany, 29 September - 3 October 1992.	E
95	SAREC-IOC Workshop on Donor Collaboration in the Development of Marine Scientific Research Capabilities in the Western Indian Ocean Region; Brussels, Belgium, 23-25 November 1993.	E
96	IOC-UNEP-WMO-SAREC Planning Workshop on an Integrated Approach to Coastal Erosion, Sea Level Changes and their Impacts; Zanzibar, United Republic of Tanzania, 17-21 January 1994.	E
96 Suppl. 1	IOC-UNEP-WMO-SAREC Planning Workshop on an Integrated Approach to Coastal Erosion, Sea Level Changes and their Impacts; *Submitted Papers* 1. Coastal Erosion; Zanzibar, United Republic of Tanzania 17-21 January 1994.	E
96 Suppl. 2	IOC-UNEP-WMO-SAREC Planning Workshop on an Integrated Approach to Coastal Erosion, Sea Level Changes and their Impacts; *Submitted Papers* 2. Sea Level; Zanzibar, United Republic of Tanzania 17-21 January 1994.	E
97	IOC Workshop on Small Island Oceanography in Relation to Sustainable Economic Development and Coastal Area Management of Small Island Development States; Fort-de-France, Martinique, 8-10 November, 1993.	E
98	CoMSBlack '92A Physical and Chemical Intercalibration Workshop; Erdemli, Turkey, 15-29 January 1993.	E
99	IOC-SAREC Field Study Exercise on Nutrients in Tropical Marine Waters; Mombasa, Kenya, 5-15 April 1994.	E
100	IOC-SOA-NOAA Regional Workshop for Member States of the Western Pacific - GODAR-II (Global Oceanographic Data Archeology and Rescue Project); Tianjin, China, 8-11 March 1994.	E
101	IOC Regional Science Planning Workshop on Harmful Algal Blooms; Montevideo, Uruguay, 15-17 June 1994.	E
102	First IOC Workshop on Coastal Ocean Advanced Science and Technology Study (COASTS); Liège, Belgium, 5-9 May 1994.	E
103	IOC Workshop on GIS Applications in the Coastal Zone Management of Small Island Developing States; Barbados, 20-22 April 1994.	E
104	Workshop on Integrated Coastal Management; Dartmouth, Canada, 19-20 September 1994.	E
105	BORDOMER 95: Conference on Coastal Change; Bordeaux, France, 6-10 February 1995.	E
105 Suppl.	Conference on Coastal Change: Proceedings; Bordeaux, France, 6-10 February 1995	E
106	IOC/WESTPAC Workshop on the Paleographic Map; Bali, Indonesia, 20-21 October 1994.	E
107	IOC-ICSU-NIO-NOAA Regional Workshop for Member States of the Indian Ocean - GODAR-III; Dona Paula, Goa, India, 6-9 December 1994.	E
108	UNESCO-IHP-IOC-IAEA Workshop on Sea-Level Rise and the Multidisciplinary Studies of Environmental Processes in the Caspian Sea Region; Paris, France, 9-12 May 1995.	E
108 Suppl.	UNESCO-IHP-IOC-IAEA Workshop on Sea-Level Rise and the Multidisciplinary Studies of Environmental Processes in the Caspian Sea Region; *Submitted Papers*; Paris, France, 9-12 May 1995.	E
109	First IOC-UNEP CEPPOL Symposium; San José, Costa Rica, 14-15 April 1993.	E
110	IOC-ICSU-CEC Regional Workshop for Member States of the Mediterranean - GODAR-IV (Global Oceanographic Data Archeology and Rescue Project) Foundation for International Studies, University of Malta, Valletta, Malta, 25-28 April 1995.	E

No.	Title	Languages
111	Chapman Conference on the Circulation of the Intra-Americas Sea; La Parguera, Puerto Rico, 22-26 January 1995.	E
112	IOC-IAEA-UNEP Group of Experts on Standards and Reference Materials (GESREM) Workshop; Miami, U.S.A., 7-8 December 1993.	E
113	IOC Regional Workshop on Marine Debris and Waste Management in the Gulf of Guinea; Lagos, Nigeria, 14-16 December 1994.	E
114	International Workshop on Integrated Coastal Zone Management (ICZM) Karachi, Pakistan; 10-14 October 1994.	E
115	IOC/GLOSS-IAPSO Workshop on Sea Level Variability and Southern Ocean Dynamics; Bordeaux, France, 31 January 1995.	E
116	IOC/WESTPAC International Scientific Symposium on Sustainability of Marine Environment: Review of the WESTPAC Programme, with Particular Reference to ICAM Bali, Indonesia, 22-26 November 1994.	E
117	Joint IOC-CIDA-Sida (SAREC) Workshop on the Benefits of Improved Relationships between International Development Agencies, the IOC and other Multilateral Intergovernmental Organizations in the Delivery of Ocean, Marine Affairs and Fisheries Programmes; Sidney B.C., Canada, 26-28 September 1995.	E
118	IOC-UNEP-NOAA-Sea Grant Fourth Caribbean Marine Debris Workshop; La Romana, Santo Domingo, 21-24 August 1995.	E
119	IOC Workshop on Ocean Colour Data Requirements and Utilization; Sydney B.C., Canada, 21-22 September 1995.	E
120	International Training Workshop on Integrated Coastal Management; Tampa, Florida, U.S.A., 15-17 July 1995.	E
121	Atelier régional sur la gestion intégrée des zones littorales (ICAM); Conakry, Guinée, 12-22 décembre 1995.	F
122	IOC-EU-BSH-NOAA-(WDC-A) International Workshop on Oceanographic Biological and Chemical Data Management Hamburg, Germany, 20-23 May 1996.	E
123	Second IOC Regional Science Planning Workshop on Harmful Algal Blooms in South America; Mar del Plata, Argentina, 30 October - 1 November 1995.	E, S
124	GLOBEC-IOC-SAHFOS-MBA Workshop on the Analysis of Time Series with Particular Reference to the Continuous Plankton Recorder Survey; Plymouth, U.K., 4-7 May 1993.	E
125	Atelier sous-régional de la COI sur les ressources marines vivantes du Golfe de Guinée ; Cotonou, Bénin, 1-4 juillet 1996.	F
126	IOC-UNEP-PERSGA-ACOPS-IUCN Workshop on Oceanographic Input to Integrated Coastal Zone Management in the Red Sea and Gulf of Aden Jeddah, Saudi Arabia, 8 October 1995.	E
127	IOC Regional Workshop for Member States of the Caribbean and South America GODAR-V (Global Oceanographic Data Archeology and Rescue Project); Cartagena de Indias, Colombia, 8-11 October 1996.	E only
128	Atelier IOC-Banque Mondiale-Sida/SAREC-ONE sur la Gestion Intégrée des Zones Côtières ; Nosy Bé, Madagascar, 14-18 octobre 1996.	E, F
129	Gas and Fluids in Marine Sediments, Amsterdam, the Netherlands; 27-29 January 1997.	E
130	Atelier régional de la COI sur l'océanographie côtière et la gestion de la zone côtière ; Moroni, RFI des Comores, 16-19 décembre 1996.	F
131	GOOS Coastal Module Planning Workshop; Miami, USA, 24-28 February 1997.	E
132	Third IOC-FANSA Workshop; Punta-Arenas, Chile, 28-30 July 1997	S/E
133	Joint IOC-CIESM Training Workshop on Sea-level Observations and Analysis for the Countries of the Mediterranean and Black Seas; Birkenhead, U.K., 16-27 June 1997.	E
134	IOC/WESTPAC-CCOP Workshop on Paleogeographic Mapping (Holocene Optimum); Shanghai, China, 27-29 May 1997.	E
135	Regional Workshop on Integrated Coastal Zone Management; Chabahar, Iran; February 1996.	E
136	IOC Regional Workshop for Member States of Western Africa (GODAR-VI); Accra, Ghana, 22-25 April 1997.	E
137	GOOS Planning Workshop for Living Marine Resources, Dartmouth, USA; 1-5 March 1996.	E
138	Gestión de Sistemas Oceano-gráficos del Pacífico Oriental; Concepción, Chile, 9-16 de abril de 1996.	S
139	Sistemas Oceanográficos del Atlántico Sudoccidental, Taller, TEMA; Furg, Rio Grande, Brasil, 3-11 de noviembre de 1997.	S
140	IOC Workshop on GOOS Capacity Building for the Mediterranean Region; Valletta, Malta, 26-29 November 1997.	E
141	IOC/WESTPAC Workshop on Co-operative Study in the Gulf of Thailand: A Science Plan; Bangkok, Thailand, 25-28 February 1997.	E
142	Pelagic Biogeography ICoPB II. Proceedings of the 2nd International Conference. Final Report of SCOR/IOC Working Group 93; Noordwijkerhout, The Netherlands, 9-14 July 1995.	E
143	Geosphere-biosphere coupling: Carbonate Mud Mounds and Cold Water Reefs; Gent. Belgium, 7–11 February 1998.	E
144	IOC-SOPAC Workshop Report on Pacific Regional Global Ocean Observing Systems; Suva, Fiji, 13-17 February 1998.	E
145	IOC-Black Sea Regional Committee Workshop: 'Black Sea Fluxes' Istanbul, Turkey, 10-12 June 1997	E